

THE UNIVERSITY OF MANITOBA

THE INFLUENCE OF MICROSTRUCTURE ON
THE STRESS CORROSION BEHAVIOUR OF
7004 Al-Zn-Mg ALLOY

by

© SPYRIDON YANNAKOPOULOS

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THE INFLUENCE OF MICROSTRUCTURE ON THE STRESS CORROSION
BEHAVIOUR OF 7004 Al-Zn-Mg ALLOY

BY

SPYRIDON YANNACOPOULOS

A thesis submitted to the Faculty of Graduate Studies of
the University of Manitoba in partial fulfillment of the requirements
of the degree of

DOCTOR OF PHILOSOPHY

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ABSTRACT

The behaviour of high strength aluminum alloys under stress-corrosion conditions has been studied extensively in recent years. In the present investigation the effect of microstructures produced by various thermal treatments on hardness and tensile properties and also on the stress corrosion cracking behaviour of high purity AA7004 aluminum alloy with and without Zr addition has been studied.

The following experimental techniques were used:

- (i) hardness measurement
- (ii) tensile testing
- (iii) optical and electron metallography
- (iv) slow strain rate testing
- (v) scanning electron microscopy
- (vi) differential scanning calorimetry

Two alloys were used in this study, one without zirconium, alloy 4, and one containing 0.15 weight percent zirconium, alloy 5. Both alloys were solution heat treated at 773K [500°C] for 30 minutes, cooled to room temperature at three different cooling rates and aged at 423K [150°C] and 393K [120°C] for various lengths of time.

It was found that:

1. The size of grain boundary precipitates and the width of the precipitate free zones increased as cooling rate from SHT decreased.

2. On aging at 423K [150°C] the grain boundary precipitates increased in size with aging time. However, the width of the precipitate free zones remained unchanged on aging.

3. The slow strain-rate test was a very simple and efficient technique used to establish the SCC susceptibility of aluminum alloys.

4. Susceptibility of AA7004 to SCC was most pronounced at the slowest strain-rate used, i.e. $4.1 \times 10^{-7} \text{ s}^{-1}$.

5. Slow cooling rates from the solution heat treatment temperature and additions of zirconium aided the SCC resistance of this alloy in the naturally aged condition.

6. The cooling rate from SHT had no influence on the SCC susceptibility of material peak aged at 423K [150°C].

7. The SCC resistance of AA7004 aluminum alloy having a fully recrystallized structure was higher in the overaged than in the peak aged condition.

8. The degree of recrystallization was the most important parameter of those microstructural features influencing the SCC resistance of AA7004.

9. Aging at 423K [150°C] resulted in a higher SCC resistance than aging at 393K [120°C].

10. The tensile properties were inferior when the alloy was aged at 423K [150°C] rather than at 393K [120°C].

11. The stress corrosion resistance of 7004 aluminum alloy, having a fully recrystallized structure, increases as the size of the grain boundary precipitates increases.

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CHAPTER 1 INTRODUCTION

Stress corrosion cracking (SCC) is the phenomenon of deterioration of materials due to the conjoint action of tensile stress and aggressive environment. The tensile stress may be applied or residual and the environment is system specific. For example, high strength aluminum alloys are susceptible to SCC in environments that contain chloride ions such as marine atmospheres. In general, as the strength of an aluminum alloy increases through aging treatment, the resistance to SCC decreases. Microstructural factors such as grain morphology, grain boundary precipitates, and size of precipitate free zones around grain boundaries influence the stress corrosion cracking behaviour of high strength aluminum alloys.

The SCC susceptibility of a given alloy can be determined by a number of standard tests and the latest advancement is the slow strain-rate test. This test utilizes a tension specimen which is tested in a specific environment under a constant slow strain-rate. A load deflection curve is produced and parameters such as time to failure, elongation to fracture, maximum load, reduction in area, and area under the load elongation curve are used to assess SCC susceptibility. The severity of the environmental effect can be de-

terminated by comparing the above mentioned parameters in different environments.

The objective of this investigation was to study the effect of microstructures produced by various thermal treatments and alloy additions on hardness, tensile properties and SCC behaviour of high purity AA7004 Al-Zn-Mg alloy.

CHAPTER 2 LITERATURE SURVEY

2.1. Aluminum Alloys

Aluminum alloys are replacing many metals and non-metals at an increasing rate due to the many advantages which they possess over other materials such as steel and some plastics. The main advantage of aluminum alloys is their high strength to weight ratio which makes these alloys very desirable substitutes due to energy saving considerations. Aluminum alloys can be easily produced in various shapes and forms since they can be cast, rolled, extruded or forged as is schematically shown in Figure 1. Aluminum scrap can also be recycled at a small fraction of the cost of its production from bauxite ore. To meet the requirements of various applications a number of aluminum alloys having a wide spectrum of properties are presently available. Also, research and development continues at major aluminum production centres and research institutes and new alloys are being developed to meet the increasing demand for improved properties and also to compete with new high strength steels and composite materials. As a result, a number of Al-Zn-Mg alloys with moderate to high strength levels have been developed for various applications. The physical metallurgy of these alloys is reviewed briefly in the next section.

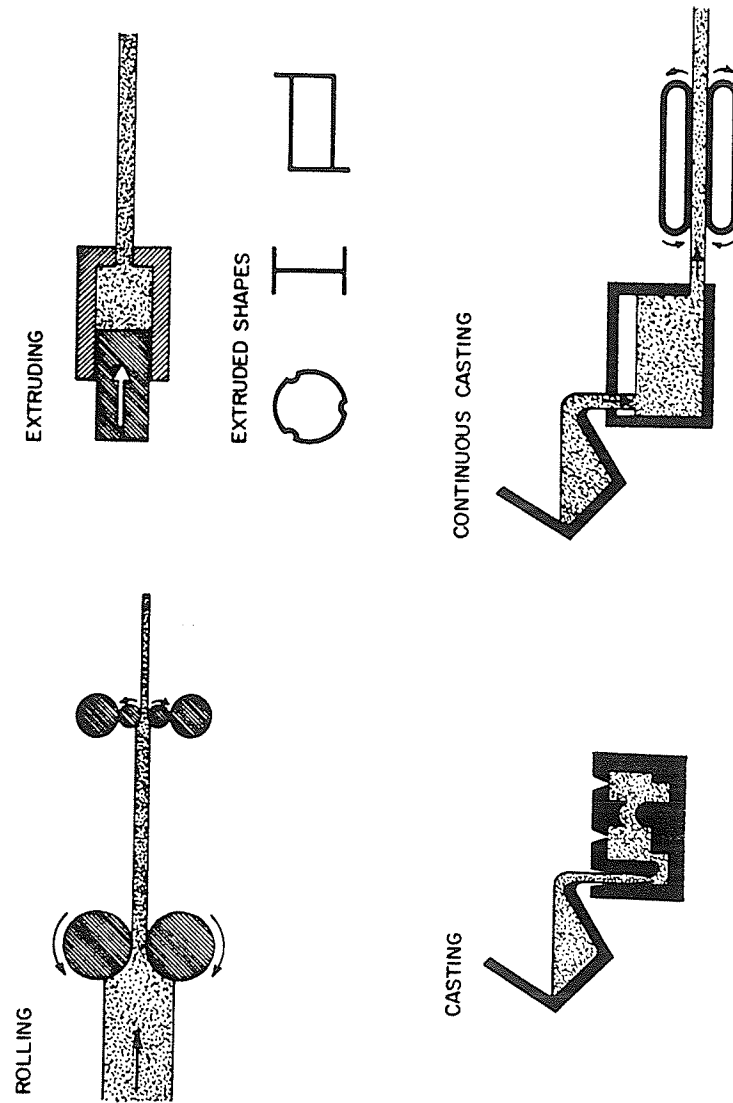


Figure 1. Schematic representation of various aluminum production methods.

2.2. Physical Metallurgy of Al-Zn-Mg Alloys

The development of the Al-Zn-Mg alloys dates back to the turn of the century. However, major investigation and research took place just prior to World War II. The bulk of research was carried out in Germany in an effort to produce copper-free aluminum alloys in accordance with the German self-sufficiency policy. At the same time, however, other industrial countries recognizing the advantages that these alloys could offer developed them and thus Al-Zn-Mg alloys became commercially available ⁽¹⁾.

Al-Zn-Mg alloys owe their popularity to a relatively high strength combined with good corrosion resistance and weldability which can be obtained even with slow quenches from the solution heat treatment temperature. It has been demonstrated that these alloys harden by precipitation of the $MgZn_2$ phase which follows the following sequence:

supersaturated solid solution $\rightarrow$ Guinier-Preston (G.P.) zones $\rightarrow \eta'$ ($MgZn_2$) $\rightarrow \eta$ ($MgZn_2$) ^(2,3).

The actual precipitation sequence depends upon the total Zn-Mg content as well as the Zn/Mg ratio. However, it has been concluded that maximum hardness is obtained when the alloy contains these elements in an atomic ratio of 2/1 ⁽⁴⁾.

Many investigators have demonstrated that the Zn + Mg content of an aluminum alloy influences its performance in aggressive environments although some disagreement exists as

to the optimum sum of zinc and magnesium which is usually fixed at approximately 6%. Also, low Mg content alloys can be extruded at lower pressures and higher speeds⁽⁵⁾, although during welding fillers containing more Mg than the parent metal must be used in order to avoid hot cracking⁽⁶⁾. Hot working properties are essentially unaffected by the Zn content^(5, 7).

2.2.1. Minor Alloy Additions of Al-Zn-Mg Alloys

Al-Zn-Mg alloys contain small amounts of transitional elements such as chromium and zirconium which inhibit recrystallization. It has been demonstrated that a non-recrystallized structure is more resistant to stress-corrosion than a fully recrystallized one. Also, the subgrain structure introduced as a consequence of these additions aids the ductility and toughness of these alloys^(8, 9). The majority of commercially available alloys contain chromium in amounts of 0.1- 0.2%. However, approximately 0.15% zirconium is added to a number of alloys either as a substitution for chromium or in addition to it. Besides being an excellent recrystallization inhibitor, Zr also improves hot cracking properties by refining the grain structure during welding⁽¹⁰⁻¹²⁾.

A controversy still exists as to the effect of copper additions. Although stress-corrosion resistance is increased

with addition of copper ⁽¹³⁾, it has been suggested that hot cracking properties of the weld may deteriorate ⁽¹⁴⁾.

2.2.2. Effect of Heat Treatment on the Microstructure of Al-Zn-Mg Alloys

All thermal treatments, from ingot homogenization to artificial aging treatment, influence the properties of Al-Zn-Mg alloys. The low solubility limit and low quench sensitivity of most of these alloys make them potentially attractive.

As stated earlier, precipitation in the Al-Zn-Mg alloys generally occurs in the following sequence:

supersaturated solid solution --> Guinier-Preston (G.P.) zones --> η' (MgZn_2) --> η (MgZn_2) ^(2,3).

G.P. zones are spherical aggregates containing Mg and Zn atoms and their size and number increase with aging temperature and time ⁽¹⁵⁾. η' is a semi-coherent intermediate phase with a hexagonal unit cell and has the following crystallographic relationship with the Al matrix:

$(10\bar{1}0) \parallel (110)$; $(0001) \parallel (1\bar{1}\bar{1})$ ⁽¹⁶⁾

The η precipitates are an incoherent equilibrium phase with a hexagonal structure and possess the form of laths or platelets ⁽¹⁷⁾.

Ingot homogenization causes re-solution of Zn and Mg which are non-uniformly distributed after solidification. During this heat treatment transition elements such as Cr and Zr tend to precipitate out ⁽¹⁸⁾.

Bichel and Bassi ⁽¹⁹⁾ have demonstrated that ingot homogenization temperature affects both the stress-corrosion and exfoliation corrosion resistance. Low homogenization temperatures (around 450°C) produce fine precipitates near the grain boundaries of the as cast structure which result in an exfoliation corrosion susceptible striated structure during subsequent deformation. However, presence of these fine precipitates inhibits recrystallization and therefore resistance of the alloy to stress-corrosion increases. High homogenization temperatures, on the other hand produce coarse precipitates and consequently the resulting microstructure consists of fully recrystallized grains which is susceptible to stress corrosion. The effect of ingot homogenization is also shown in Figure 2, which shows that the susceptibility of an Al-Zn-Mg alloy to SCC increases sharply for homogenization temperatures higher than 500°C.

The low quench sensitivity of most medium strength Al-Zn-Mg alloys allows them to be cooled very slowly from the solution heat treatment temperature without excessive loss in tensile properties, except in cases of heavy sections in which the fine sub-grain structure present at the back end

SCC - SUSCEPTIBILITY

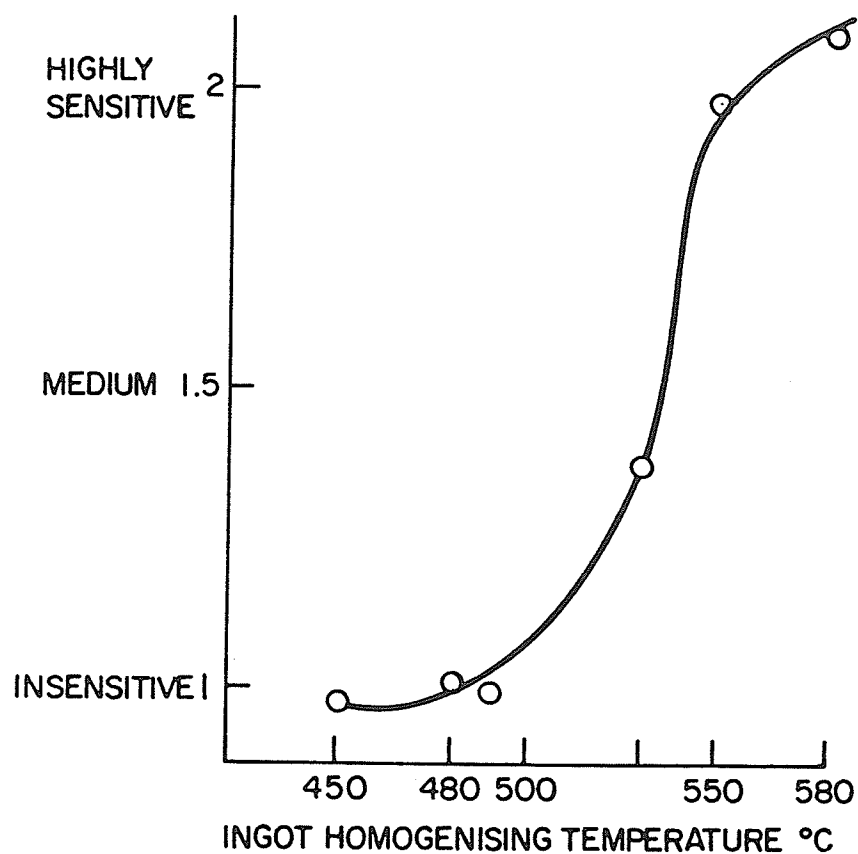


Figure 2. Effect of ingot homogenization temperature on stress corrosion susceptibility. (Water quenching after solution anneal and natural aging) ⁽¹⁹⁾

of extruded sections can result in considerable loss in strength⁽¹⁹⁾. Cooling rate from solution heat treatment also affects the stress corrosion susceptibility of these alloys and to a small extent their tensile properties. Fast cooling rates result in an increased susceptibility to stress-corrosion, whereas very slow cooling (for example less than 1°C/sec) results in a loss of strength of an experimental Al-Zn-Mg alloy⁽²⁰⁾. This effect of cooling rate on stress corrosion is attributed to the precipitate distribution at high angle boundaries. In fast quenched material the grain boundary precipitates are small (750 Å) and the precipitate free zone (PFZ) width is around 600-800 Å. However, in slowly cooled material the precipitates are about 3000 Å in size, are well spaced and the width of the PFZ is around 2000-3000 Å⁽⁴⁾. The effect of these grain boundary features on stress-corrosion resistance is attributed to the observation that stress corrosion cracks always follow high angle boundaries⁽²¹⁾.

Age hardening which is controlled by the dispersion of precipitates and their degree of coherency with the matrix lattice is the most important process controlling the properties of Al-Zn-Mg alloys. Also, the interval between quenching from solution heat treatment and artificial aging, i.e. aging at room temperature prior to artificial aging, has an important effect on the final properties of the alloy. Aging at room temperature causes solute atoms to clus-

ter and form G.P. Zones. These provide finely dispersed nucleation sites for further precipitation during artificial aging. As an alternative to room temperature aging, a slow heating rate to the artificial aging temperature or a two-stage aging treatment may be applied. In practice, aging treatments of Al-Zn-Mg alloys consist of either a single treatment of 12-24 hours at 120-135°C (usually after a period of up to 3 days of natural aging at room temperature) or a period of 4-8 hours at a temperature of 90-100°C followed by further aging of 8-16 hours at a higher final temperature in the range 150-180°C⁽⁴⁾.

The brief review of Al-Zn-Mg alloys presented above shows that these alloys have a tendency to suffer from SCC failures the extent of which depends upon several metallurgical and environmental factors. In view of the increasing applications of Al-Zn-Mg alloys it was decided to study the SCC behaviour of Al-3.8%Zn-1.8%Mg alloy, commercially known as AA7004. Therefore, in the next section stress corrosion cracking and various factors that influence it are reviewed briefly. The SCC behaviour of aluminum alloys is emphasized but related relevant results on other alloys are also included.

2.3. Stress Corrosion Cracking

Stress-corrosion cracking may be defined as the type of attack in which a tensile stress and a corrosive environment coexist⁽²²⁾. The tensile stress may be either applied or residual⁽²³⁾. Extensive studies on stress-corrosion cracking began when it was suspected that this was the cause of failure of small-arms brass cartridge cases⁽²²⁾. Ever since, failures in riveted or welded steam boilers, other welded steel structures, natural gas pipelines, stainless steel heat exchangers and other machinery components have been attributed to the damaging effect of the combination of tensile stress and a corrosive environment.

Many alloys have been found to suffer SCC under specific conditions. These alloys include stainless steels, low carbon steels, brasses, titanium alloys and aluminum alloys. Of the aluminum alloys those containing Cu (2XXX series) and Zn (7XXX series) as a major addition have been found to be susceptible to SCC in chloride-containing atmospheres. The strength properties of these alloys are obtained from heat treatment rather than cold rolling. Stress-corrosion failures have also occurred in the 5XXX series alloys containing more than 3.5% Mg and some high strength casting alloys⁽²⁴⁾.

2.3.1. Sources and Magnitude of Stress

Failures do not necessarily occur as a result of the applied design stresses. To these, however, residual stresses may be added and as a result failure occurs. Residual stresses may result from fabrication processes such as deep drawing, punching, rolling, welding, etc. Annealing of the structure subsequent to fabrication will eliminate the residual stresses, but this is often either uneconomical or impossible. Residual stresses may also be the result of corrosion products inside a crevice since their volume is much greater than the volume of the reacting substances ⁽²⁵⁾.

2.3.2. Corrosion Damage

Stress corrosion usually occurs in the presence of mild corrosive atmospheres, and surface corrosion products are almost non-detectable. If extensive corrosion occurs the component usually fails due to the loss of cross sectional area and not by SCC. It is fortunate that corrosion and SCC occur only under rather unique combinations of material-environment conditions.

2.3.3. Types of Fracture

In the early stages of stress corrosion cracking the cracks are microscopic and cannot be detected by visual ex-

amination. These cracks can be either intercrystalline or transcrystalline depending on the alloy-environment combination⁽²³⁾. Intercrystalline cracks follow the grain boundaries of the alloy and this type of cracking is usually found in aluminum alloys⁽²⁶⁾, low-carbon steels and brasses⁽²⁷⁾. Transcrystalline cracks pass through the grains of the alloy and are usually found in stainless steels⁽²⁷⁾. A combination of intercrystalline and transcrystalline cracks is possible. However, one type of cracking usually predominates.

2.3.4. Mechanisms of Stress Corrosion

During the past 10-15 years a great deal of research has been devoted to determining the processes occurring during environmentally induced failures of metals and alloys. Also, contributions have been made from investigations not directly related to the determination of such processes. Although the number of proposed models for environmentally induced crack initiation and propagation has been narrowed down to only a few (Table 1) considerable controversy still exists regarding a unifying theory which would apply to all such failures. The proposed models may be classified into two groups. The first group includes those models which are based on a chemical dissolution process playing the major role in crack initiation and propagation. The second group

TABLE 1

Environmentally Induced Crack
Propagation Models

1. Dissolution
 Film Rupture Model
2. Mechanical Fracture
 - (a) Ductile Fracture
 Tunnel Model
 - (b) Brittle Fracture
 - I. Adsorption
 - II. Hydrogen Embrittlement

includes those models which are based on mechanical fracture being primarily responsible for the failure. Furthermore, the mechanical fracture models have been grouped into those which attempt to explain failures by ductile fracture and those which attempt to explain failures by brittle fracture.

2.3.4.1. The Film-Rupture Model

The film-rupture model is representative of those models which explain crack propagation by preferential anodic dissolution and is based on the assumption that localized plastic deformation at the crack tip causes rupture of a protective surface film, thus allowing rapid anodic dissolution of the exposed surface. The crack walls remain protected by the film.

This model originated from independent work by Champion⁽²⁸⁾ and Logan⁽²⁹⁾ and has been supported by others^(30,31). The repassivation rate, or the rate at which film formation occurs, governs the crack velocity or in other words the susceptibility of a given alloy to SCC. Different views exist as to whether the passive film at the crack tip partially or completely forms between mechanical fracture and dissolution events. Champion⁽²⁸⁾ suggests that unless the protective film at the crack tip forms only partially, the alloy would become immune to SCC due to complete repassivation. This approach, therefore, supports the view

that crack propagation is a continuous process and has also been supported by others ^(32, 33). Staehle ^(30, 31) and Vermilyea ^(34, 35) have supported the view that complete repassivation of the crack tip takes place between mechanical fracture events and that creep is responsible for the protective film rupture, as was suggested by Vermilyea ⁽³⁴⁾. Bursle and Pugh ⁽³⁶⁾, however, suggest that the Champion model outlined above, modified to include slip-step emergence, presents a more reasonable model for crack propagation in passivating solutions.

2.3.4.2. The Tunnel Model

Swann et. al. ^(37 38) first proposed the tunnel model which is based on the idea that crack propagation takes place by ductile fracture rather than dissolution or brittle mechanical fracture. This model suggests that cracking initiates at slip steps by formation of fine corrosion tunnels which grow in length and diameter and eventually join by ductile fracture of the metal ligaments between them (Figure 3) ⁽³⁶⁾. Crack propagation takes place by repeated tunnel formation and growth followed by ductile rupture. This model applies to transgranular cracking only and evidence has been found in transgranular SCC of austenitic stainless steels ⁽³⁹⁾.

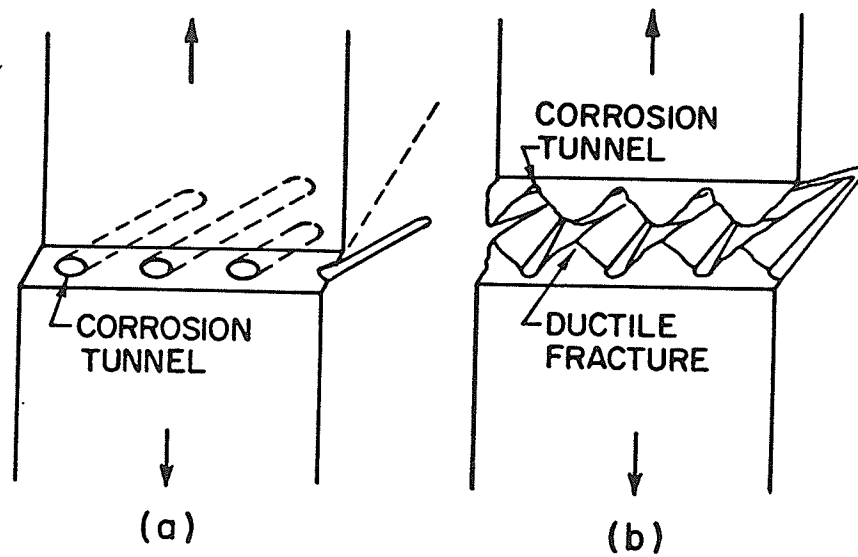


Figure 3. Schematic of tunnel model, showing the initiation of a crack by the formation of corrosion tunnels at a slip step and the subsequent rupture of the metal ligaments ⁽³⁶⁾

2.3.4.3. The Adsorption Model

Of the brittle fracture models, the adsorption model is based on the assumption that specific species are absorbed which interact with strained bonds at the crack tip. As a result of this interaction the bond strength is reduced and brittle fracture may result at low stresses. This concept of adsorption-induced bond strength reduction has been applied to SCC^(40,41) and corrosion fatigue⁽⁴²⁾ as well as hydrogen embrittlement⁽⁴³⁾.

2.3.4.4. Hydrogen Embrittlement

The phenomenon of hydrogen embrittlement is well known and occurs in a wide variety of materials such as alloy steels, titanium alloys, stainless steels, and some aluminum alloys. However, the role of hydrogen in SCC still remains highly controversial. The original model by Troiano⁽⁴⁴⁾ postulates that hydrogen penetrates deep below the surface and also that cracking is discontinuous. Oriani⁽⁴⁵⁾, however, considers that embrittlement takes place only within a few atomic distances from the surface and that cracking is essentially continuous on a macroscopic scale.

It is believed that in some alloys hydrogen embrittlement occurs by the formation of a brittle hydride phase. For example a titanium alloy having the Widmanstätten microstruc-

ture underwent slow crack growth in hydrogen gas at one atmosphere. Cracking followed the α - β interface and a layer of FCC titanium hydride was identified at the fracture surfaces⁽⁴⁶⁾. Hydrogen embrittlement by hydride formation may also be applicable in alloys containing other hydride forming elements such as vanadium⁽⁴⁷⁾, niobium⁽⁴⁸⁾ and zirconium⁽⁴⁹⁾ but it is doubtful that this model extends to systems such as high strength steels, austenitic stainless steels and aluminum alloys. In these systems a decohesion model based on the assumption that the presence of hydrogen in the lattice reduces the cohesive strength of the atoms thereby inducing brittle fracture is generally supported^(44,45). For example, numerous observations suggest that intergranular SCC of Al-Zn-Mg alloys is due to hydrogen embrittlement⁽⁵⁰⁾ despite the view that the film-rupture mechanism for the SCC of high strength aluminum alloys has been strongly supported⁽⁵¹⁾.

2.3.5. Effect of Directionality on Stress Corrosion Behaviour

Invariably, production of metals and alloys involves forming processes such as rolling, forming, pressing and extrusion which introduce residual stresses as well as an anisotropy of properties. That is, the properties vary with direction of load application. One of the factors which in-

fluences the strength of an alloy is the grain orientation in the structure. In general, an alloy exhibits higher strength when a tensile load is applied parallel to the long axis of the grains. Susceptibility of aluminum alloys to SCC is higher when tensile stresses are applied perpendicular to the long axis of the grains. In this case a crack formed on the elongated boundary of one grain may join a crack formed at the boundary of the next grain and crack propagation is accelerated in this fashion. However, when a tensile stress is applied along the rolling or extrusion direction the short grain boundaries which are attacked do not link up easily with attacked boundaries of adjacent grains. In this case the SCC attack is milder, since individual grain boundaries are attacked but they do not join to form a main crack ⁽²⁴⁾.

2.3.6. Effect of Alloy Additions on Stress Corrosion Behaviour of Al-Zn-Mg Alloys

The chemical and mechanical properties of aluminum alloys are mainly due to the alloying elements which are added to pure aluminum or are present as impurities. During heat treatment alloying elements combine with Al or other elements to form second phases. Common additions to the Al-Zn-Mg alloys include copper, chromium, iron, manganese, silicon, titanium and zirconium.

Chromium is added in amounts up to 1% because of its beneficial effect on SCC resistance. The phase in equilibrium with Al is usually designated as CrAl_7 (21.6% Cr). Some Cr bearing ternary compounds such as $\text{Cr}_2\text{Mg}_3\text{Al}_{25}$ and $(\text{CrMn})\text{Al}_{12}$ can also form⁽⁵²⁾. Cr induces uniformity of precipitation throughout the alloy⁽¹⁵⁾.

Copper is one of the most common additions to the ternary Al-Zn-Mg system. New phases are not formed by the additions of copper. Every one percent addition of copper lowers the upper and lower freezing point by some 10-15 and 25-30°C respectively⁽⁵²⁾. It extends the stability of G.P. zones, but increases the rate of growth of η' precipitates⁽¹⁵⁾.

Iron is not usually added to Al alloys, but it is a common impurity. The phase in equilibrium with Al is usually found to be FeAl_3 . Iron may form ternary or quaternary compounds with Cu, Mg, Mn, Ni and Si but none of them are normally present in the Al-Zn-Mg alloys⁽⁵²⁾.

During development of the aluminum industry it was realized that the corrosive effect of iron could be minimized by additions of manganese. Manganese combines with iron to form phases such as $(\text{FeMn})\text{Al}_6$ and $(\text{CuFeMn})\text{Al}_6$ which are well dispersed in the matrix.

Like iron, silicon is present in small quantities (<0.6%) as an impurity and is not known to provide any benefits at these low concentrations⁽⁵²⁾.

The well known grain refining properties of titanium have been used in aluminum alloys. Additions of Ti induce the formation of TiC or TiAl_3 . These compounds are finely dispersed in the matrix and provide nucleation sites for the formation of Al crystals during cooling.

Stress corrosion cracking failures in aluminum alloys are invariably intergranular and, therefore, a non-recrystallized coarse grained microstructure, i.e. minimum of grain boundaries, is more resistant to SCC than a fully recrystallized microstructure. It has been demonstrated that additions of recrystallization retarding elements such as zirconium in amounts of up to 0.15% aid the SCC resistance of aluminum alloys ⁽⁵³⁻⁵⁶⁾.

2.3.7. Effect of Microstructure on Stress Corrosion Behaviour of Al-Zn-Mg Alloys

Heat treatment controls the microstructure which in turn has a great influence on the stress corrosion cracking susceptibility of Al-Zn-Mg alloys. Generally, those microstructural factors which influence the resistance to SCC include the grain size, the degree of recrystallization, the dislocation structure produced by cooling, the matrix precipitate structure, the size and distribution of grain boundary precipitates, and the width of the precipitate free zones. The rate of cooling from the solution heat-treatment temperature

is also a very important factor in determining the SCC resistance of aluminum alloys. A rapid quench is detrimental to SCC resistance ⁽⁵⁴⁾. It has been suggested that rapid quenching results in a high vacancy concentration at the grain boundaries, which provides nucleation sites for pearl-necklace type grain boundary precipitates ^(55, 57). It is believed that these grain boundary precipitates are anodic to the aluminum oxide surface and are attacked electrochemically in corrosive environments. Slower cooling, however, results in well spaced grain boundary precipitates which are not detrimental to SCC resistance. It has been shown, that the size and shape of the matrix precipitates influence the mechanical properties and general corrosion behaviour but not the SCC resistance. However, the grain boundary precipitates influence the SCC life a great deal, and as the spacing of the grain boundary precipitates increases the stress corrosion cracking life also increases ⁽⁵⁵⁾. Since the crack propagation is retarded or prevented in the absence of grain boundaries, a non-recrystallized structure results in an increase of SCC resistance ⁽⁵⁵⁾. Prevention of recrystallization can be achieved by additions of zirconium, and hence, the addition of Zr improves the SCC resistance.

The size and distribution of precipitates in the Al-Zn-Mg alloys have a great influence on the SCC susceptibility, although some disagreement exists. In general the following conclusion has been drawn: susceptibility of these alloys

to SCC decreases as the matrix and grain boundary precipitate size increases, as the grain boundary precipitate spacing increases, and as the precipitate free zone width increases^(2,3). The size, type and spacing of the matrix precipitates may control susceptibility to SCC through their effect on the deformation process^(5,8).

2.4. Scope of This Research

The above review of the literature suggests that the stress corrosion behaviour of Al-Zn-Mg alloys is influenced by many microstructural factors. Also, it is evident that generalizations cannot be made concerning aluminum alloys and that the stress corrosion behaviour is system specific. High purity AA7004 is an experimental alloy and little is known concerning its properties. In view of this it was decided to determine first the aging kinetics of this alloy during aging at 423K [150°C] and 393K [120°C] and subsequently to study the behaviour of this alloy under stress corrosion cracking conditions in 3.5% NaCl solution at room temperature using the slow strain-rate technique.

CHAPTER 3 EXPERIMENTAL TECHNIQUES

3.1. Materials

The chemical composition of high purity 7004 aluminum alloy with and without zirconium used in this study is shown in Table 2. The 4mm thick and 127mm wide extruded plates of the alloys were supplied by ALCAN Ltd., Kingston, Ontario.

3.2. Heat Treatment Procedure

The heat treatment schedule consisted of solution heat treating samples at 773K [500°C] for 30 minutes followed by cooling to room temperature at the following cooling rates which are also shown in Table 3.

- (1). water quenching
- (2). air cooling at 0.77°C/sec.
- (3). air cooling samples between two 25mm aluminum blocks at 0.06°C/sec.

The solution heat treated specimens were given a natural aging treatment for 16 hours which was followed by artificial aging at 393K [120°C] or 423K [150°C] for various lengths of time.

TABLE 2

CHEMICAL COMPOSITION OF 7004 (wt%)

ALLOY	Zn	Mg	Zr	Cu	Fe	Mn	Si	Al
4	3.88	1.59	<0.01	<0.01	<0.01	<0.01	<0.01	bal.
5	4.13	1.77	0.15	<0.01	<0.01	<0.01	<0.01	bal.

TABLE 3

COOLING FROM SHT TEMPERATURE

COOLING METHOD	COOLING RATE
	$^{\circ}\text{C}/\text{sec.}$
Water Quenching	--
Air Cooling	0.77
Air Cooling in Block	0.06

In more detail, the following heat treatment schedules, which are also shown in Table 4, were employed:

A. Flat tensile specimens with 20mm gauge length, which were parallel with the long-transverse extrusion direction, were cut and then polished with 600 grade paper. Both alloys were then solution heat treated at 773K [500°C] for 30 minutes and water quenched to room temperature. They were then naturally aged for 16 hours followed by artificial aging at 423K [150°C] for up to 1000 hours.

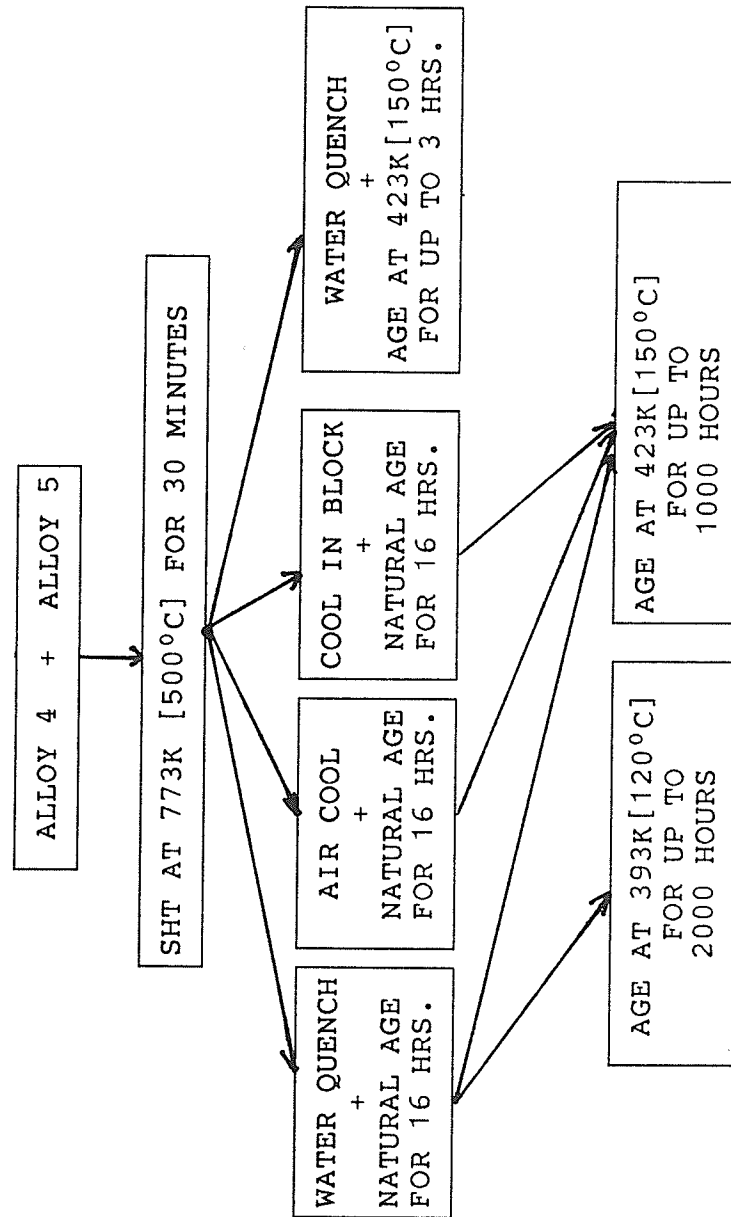
B. Same as schedule A, but specimens were air cooled to room temperature from solution heat treatment. The cooling rate was measured to be 0.77°C/sec.

C. Same as schedule A, but specimens were cooled in 25mm thick aluminum blocks to room temperature from solution heat treatment. The cooling rate was measured to be 0.06°C/sec.

D. Same as schedule A, but specimens were aged at 423K [150°C] immediately after water quenching, without natural aging, for up to 3 hours.

E. Same as schedule A, but specimens were aged at 393K [120°C] for up to 2000 hours.

TABLE 4
HEAT TREATMENT SCHEDULE



3.3. Hardness Measurements

Hardness measurements were taken after each heat treatment using a Vickers hardness tester and a 10 kilogram load. Hardness values were taken as an average of five readings.

3.4. Tensile Testing

All tensile tests were carried out at room temperature. Flat tensile samples with 20mm gauge length were tested in an Instron testing machine at an initial strain-rate of $4.1 \times 10^{-4} \text{s}^{-1}$. All tensile samples were stored at 250K [-23°C] after heat treatment before testing at ambient temperature.

3.5. Optical Metallography

Samples of both alloys were polished using standard techniques and then etched with a solution of 2.5% HNO_3 , 1.5% HCl , 1% HF and 95% distilled H_2O . Optical observations were made and photomicrographs of the microstructures were taken using a Nikon metallograph.

3.6. Transmission Electron Microscopy

The microstructure of the aged material was examined by thin film electron microscopy in a Philips 300 transmission electron microscope. Slices approximately 0.3mm thick were

cut from the grip portion of the heat treated tensile specimens using a diamond wheel cut-off saw and thinned on 600 grade paper to 0.15mm. 3mm diameter discs were punched from these slices and electropolished in a Tenupol Struers unit. Electropolishing at 12 Volts and 35 mA was carried out in a 5% perchloric acid and 95% methyl-alcohol bath maintained at approximately 235K [-38°C].

3.7. Differential Scanning Calorimetry

A DuPont 9900 DSC was used for the calorimetric study. Discs weighing approximately 1 gram were heated between 293 [20] and 433K [160°C] at a rate of 283K [10°C] per minute in a nitrogen gas atmosphere.

3.8. Stress Corrosion Testing

Stress-corrosion cracking is a little understood subject and despite a great deal of research no standards have been set which can be used directly in materials selection and design. Also, the behaviour under stress-corrosion conditions is unique for every material-environment system due to the great number of variables which influence the behaviour. Therefore, detailed testing is required under conditions identical to those anticipated in service before a component is put into application. A number of standard tests are

available. The most common ones are the boiling 3.5% NaCl in water and the alternate immersion test both of which determine the time to failure and are used mainly for comparative purposes. Other tests, such as the static load cantilever-beam and the constant displacement wedge-opening-loading are used mainly for crack propagation and fracture toughness determination under conditions which promote SCC.

The slow strain-rate test is the latest advancement in SCC studies. The test utilizes a tension specimen which is tested at a constant "slow" strain-rate. Compared to the tests mentioned earlier, the slow strain-rate test requires considerably shorter times. The choice of strain-rate is important and critical and not all systems respond similarly to similar strain-rates. Even if an alloy is known to be susceptible to SCC in a certain environment, ductile failure of this alloy may occur during slow strain-rate testing if the strain-rate is too high for the chemical reactions necessary for SCC. On the other hand, it is also possible that the strain-rate is too slow to promote stress-corrosion cracking. Therefore, when a new system is tested for SCC a wide range of strain-rates must be used. A load-extension curve is produced during the slow strain-rate test as in the case of a simple tension test. Parameters such as time to failure, elongation to fracture, reduction in area, and area under the load-elongation curve are used to assess SCC susceptibility of an alloy. The severity of the environmental

effect can be determined by comparing the tensile properties with and without the presence of the environment ^(59,60) .

In this investigation, flat tensile specimens identical to those used for tensile testing representing all heat treatments, except those not naturally aged, were tested at initial strain-rates between 4.1×10^{-4} and 4.1×10^{-7} sec^{-1} . One sample in each heat treatment condition was tested in silicone oil and one in a 3.5%, by weight, solution of NaCl in water. A linear polyethylene container was used to retain approximately one litre of solution around the gauge section of the sample. Silicone sealant was used to seal the container-specimen interface. Small amounts of distilled water were added daily to compensate for evaporation losses in the case of the 3.5% NaCl tests.

3.9. Scanning Electron Microscopy

The fracture surfaces of a selected number of slow strain-rate specimens were examined in an ASI Super Mini Scanning Electron Microscope. Small pieces containing the fracture surfaces of these samples were mounted on cylindrical aluminum holders with the aid of silver-paste glue for good electrical conductivity. The fracture surfaces were examined using the secondary electron mode in order to compare the fracture characteristics of specimens tested in silicone oil and 3.5% NaCl solution.

CHAPTER 4 EXPERIMENTAL RESULTS

AA7004 aluminum-zinc-magnesium alloy is a relatively new entry into the medium strength aluminum alloy field. Therefore, the influence of aging on the microstructure and mechanical properties has not yet been reported. As a result it was decided to establish the aging behaviour of the alloy before studying its stress-corrosion cracking behaviour. In this chapter the aging kinetics as studied by hardness measurements, tensile testing and metallography, are presented. These results are followed by the stress-corrosion cracking behaviour of the alloy and the fracture surface observations.

4.1. Aging Behaviour of 7004 Al-Zn-Mg Alloy

The material was solution heat treated at 773K [500°C] followed by cooling at various rates, as described in Chapter 3, and then aged at 423K [150°C] and 393K [120°C] for various lengths of time. The aging kinetics were studied by hardness and tensile properties and the microstructures of the solution heat treated and aged specimens were examined by optical and electron metallography.

TABLE 5

Effect of Aging Time on Hardness
of Alloys 4 and 5

HARDNESS (VPN), μ , AND STANDARD DEVIATION, σ					
AGING TEMPERATURE		423K[150°C]		393K[120°C]	
AGING TIME		ALLOY 4	ALLOY 5	ALLOY 4	ALLOY 5
As Quenched	μ	45.5	48.6	45.5	48.6
	σ	0.9	1.5	0.9	1.5
As Quenched +16 h RT	μ	68.3	70.0	68.3	70.0
	σ	1.2	1.3	1.2	1.3
5 min	μ	47.4	48.2	61.8	59.9
	σ	0.4	0.6	0.4	1.4
10 min	μ	45.0	47.5	50.9	52.9
	σ	0.4	1.1	1.7	0.8
15 min	μ	46.5	49.3	49.4	51.9
	σ	0.8	0.4	1.5	0.7
1 hour	μ	53.4	51.3	52.1	53.6
	σ	3.6	0.7	2.1	0.8
2 hours	μ	60.1	59.8	60.5	61.0
	σ	0.7	0.7	1.3	2.7
3 hours	μ	74.8	80.7	64.6	64.8
	σ	3.8	6.1	1.7	1.5
5 hours	μ	83.8	84.2	71.4	69.2
	σ	1.8	1.7	1.2	1.7
10 hours	μ	97.0	99.1	86.5	79.5
	σ	1.7	1.7	1.0	2.2
24 hours	μ	106.4	106.4	100.3	98.4
	σ	2.7	1.9	2.9	1.6
100 hours	μ	102.0	95.7	125.2	127.2
	σ	2.0	1.6	2.7	2.6
300 hours	μ	97.7	93.1	137.2	133.3
	σ	1.4	1.6	1.3	2.4
600 hours	μ	--	--	135.4	133.4
	σ	--	--	2.1	1.8
1000 hours	μ	87.7	88.4	132.6	126.6
	σ	1.4	1.0	1.5	1.8
2000 hours	μ	--	--	124.8	124.4
	σ	--	--	2.4	2.3

4.1.2 Aging Kinetics

4.1.2.1. Aging at 423K [150°C]

The influence of aging time on the hardness of alloys 4 and 5 was determined by solution heat treating specimens at 773K [500°C] for 30 minutes, water quenching to room temperature, room temperature aging for 16 hours followed by artificial aging at 423K [150°C] for various lengths of time. It was observed that an initial decrease in hardness from 70 to about 50 VPN took place after approximately 10 minutes of aging. The hardness of both alloys, however, increased to 106 VPN after aging for 24 hours. On further aging the hardness dropped to 87 VPN after 1000 hours, as shown in Table 5 and Figure 4.

A similar trend to that for hardness was also reflected by the variation in the yield and ultimate strength with aging time for both alloys. When alloy 4 was aged at 423K [150°C] its yield strength decreased from 108.2 to 63.6 MPa after 10 minutes of aging. It increased, however, to 276.5 MPa after 24 hours and then decreased to 194.8 MPa on further aging for 1000 hours. The ultimate tensile strength of the same alloy decreased from 237.3 to 184.4 MPa after 10 minutes and it then increased to 312.2 MPa after 24 hours. On further aging, however, for 1000 hours at 423K [150°C] the ultimate tensile strength decreased to 255.6 MPa. The

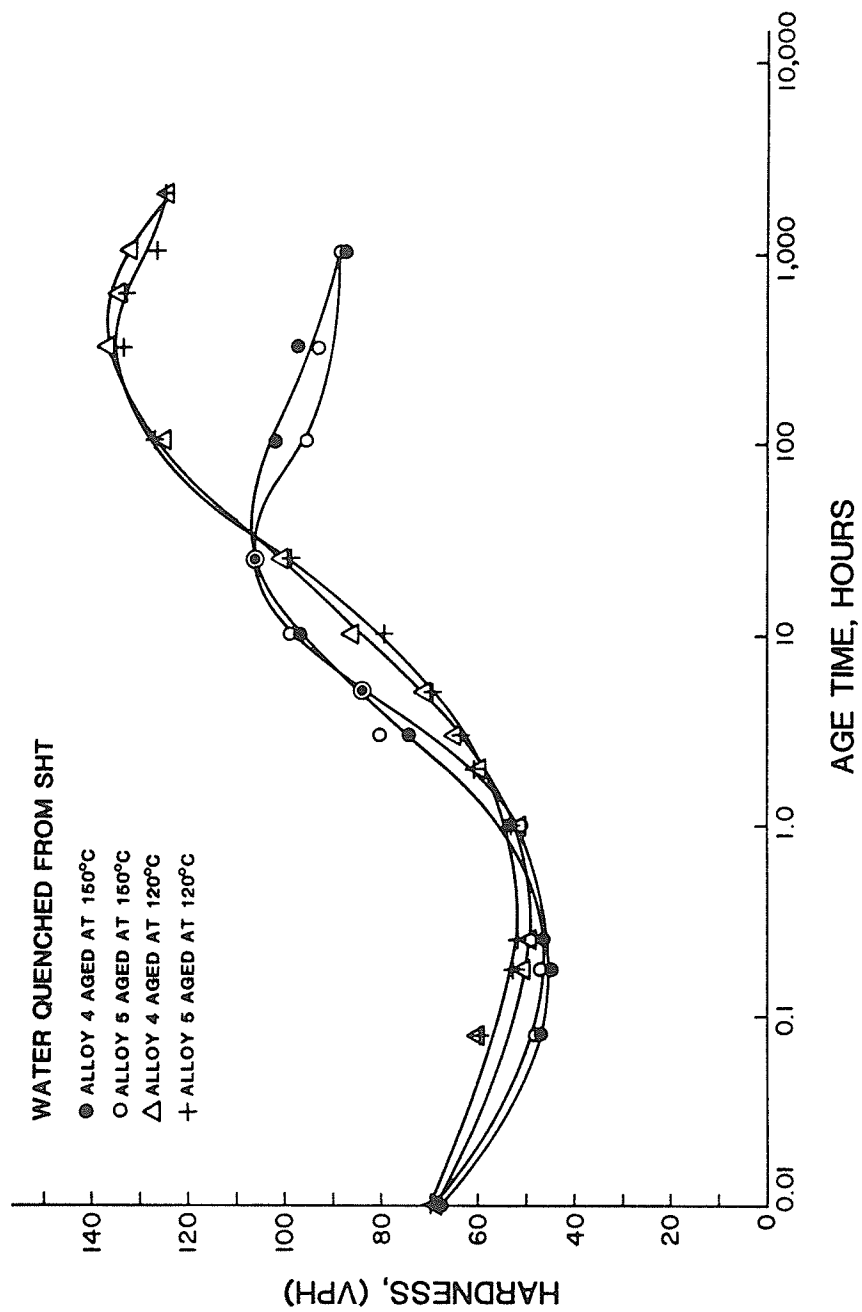


Figure 4. Effect of aging time on hardness of alloys 4 and 5.

elongation of alloy 4 increased from 39.3 to 42.1% after 10 minutes of aging and then decreased to 13.5% after 24 hours. It increased, however, to 28% after aging at 423K [150°C] for 1000 hours, as shown in Table 6 and Figure 5. The same behaviour was observed when alloy 5 was aged at 423K [150°C]. An initial decrease in the yield strength from 118.1 to 63.2 MPa was observed after 10 minutes which was followed by an increase to 264.1 MPa after 24 hours. Once again the yield strength decreased to 197.1 MPa after 1000 hours of aging. The initial drop in the ultimate tensile strength from 250.8 to 189.5 MPa after 10 minutes was followed by an increase to 314 MPa after 24 hours. However, on further aging for 1000 hours the ultimate tensile strength decreased to 267 MPa. The percentage elongation to fracture increased from 38.6 to 46.1% after 10 minutes of aging but then gradually decreased to 21.2% after 24 hours. It increased, however, to 27.3% on further aging for 1000 hours, as illustrated in Table 6 and Figure 6.

To investigate the cause of the initial softening that occurs on aging, both alloys 4 and 5 were artificially aged at 423K [150°C] without any prior natural aging. The results are given in Table 7 and Figure 7. It was observed that the hardness of the zirconium-containing alloy 5 remains fairly constant on aging up to 3 hours. However, the hardness of the zirconium free alloy 4 exhibits a slight increase from 45.5 to 56.7 VPN after 3 hours of aging at 423K [150°C].

TABLE 6

Tensile Properties of Alloys 4 and 5,
Aged at 423K[150°C]

HEAT TREATMENT	ALLOY	σ_y (MPa)	σ_u (MPa)	%El
As Quenched	#4	51.5	173.9	45.5
	#5	69.1	194.6	43.1
As Quenched +16h RT	#4	108.2	237.3	39.3
	#5	118.1	250.8	38.6
5 min	#4	63.6	187.5	43.7
	#5	69.5	195.8	44.3
10 min	#4	63.6	184.4	42.1
	#5	63.2	189.5	46.1
15 min	#4	67.2	191.0	31.7
	#5	76.5	201.0	39.6
1 hour	#4	101.0	211.3	38.5
	#5	89.6	201.5	38.3
2 hours	#4	139.0	227.4	29.4
	#5	115.9	218.9	36.4
3 hours	#4	173.7	251.2	25.6
	#5	150.7	254.5	26.4
5 hours	#4	206.9	269.2	26.9
	#5	188.0	265.5	24.0
10 hours	#4	249.5	300.1	17.1
	#5	232.1	291.0	15.3
24 hours	#4	276.5	312.2	13.5
	#5	264.1	315.6	21.2
100 hours	#4	281.8	337.0	18.1
	#5	263.7	314.0	20.9
300 hours	#4	221.2	278.0	20.8
	#5	202.8	270.5	25.6
600 hours	#4	--	--	--
	#5	--	--	--
1000 hours	#4	194.8	255.6	28.0
	#5	197.1	267.0	27.3

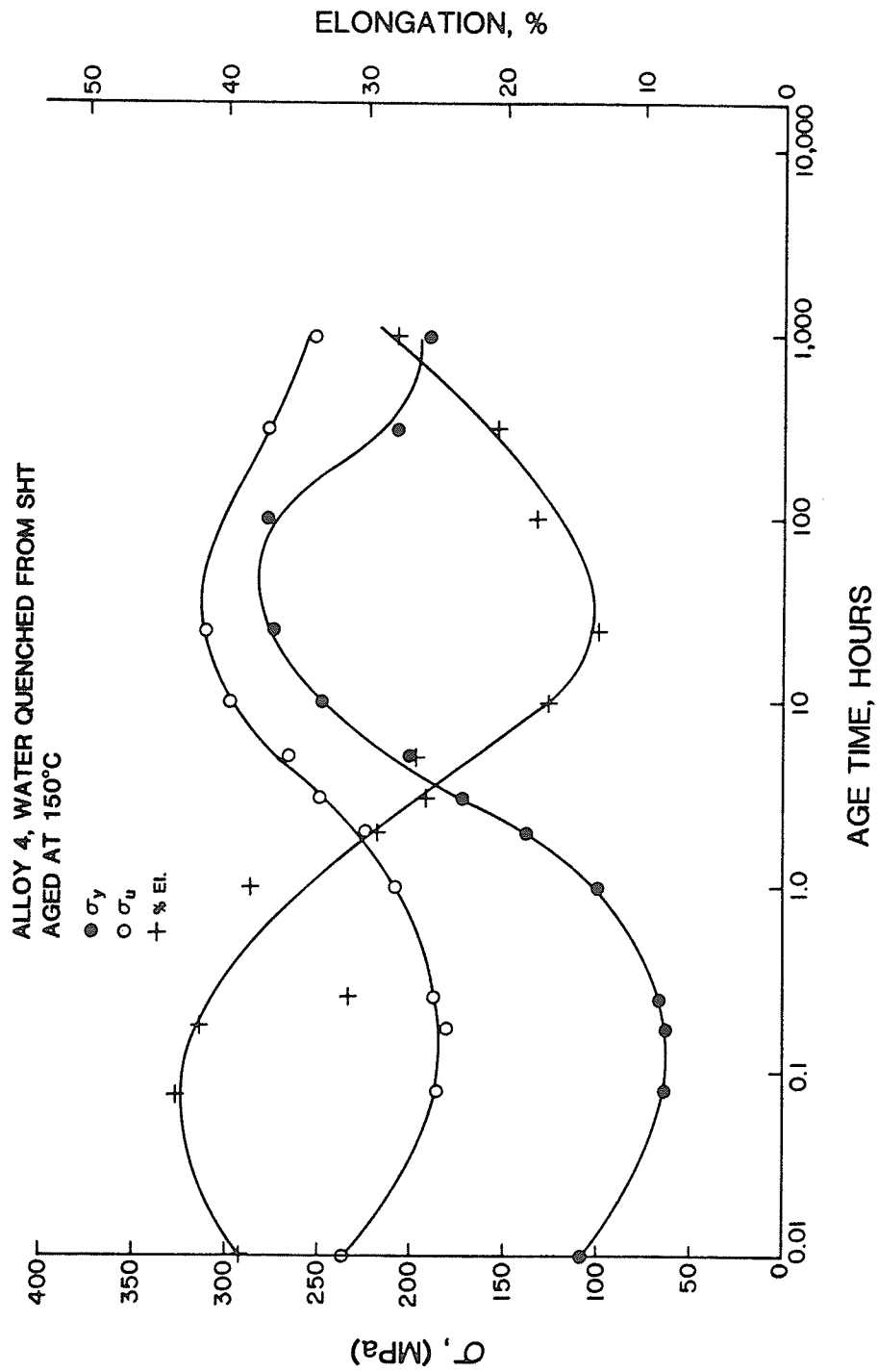


Figure 5. Effect of aging time on tensile properties of alloy 4 water quenched from SHT and aged at 423K [150°C].

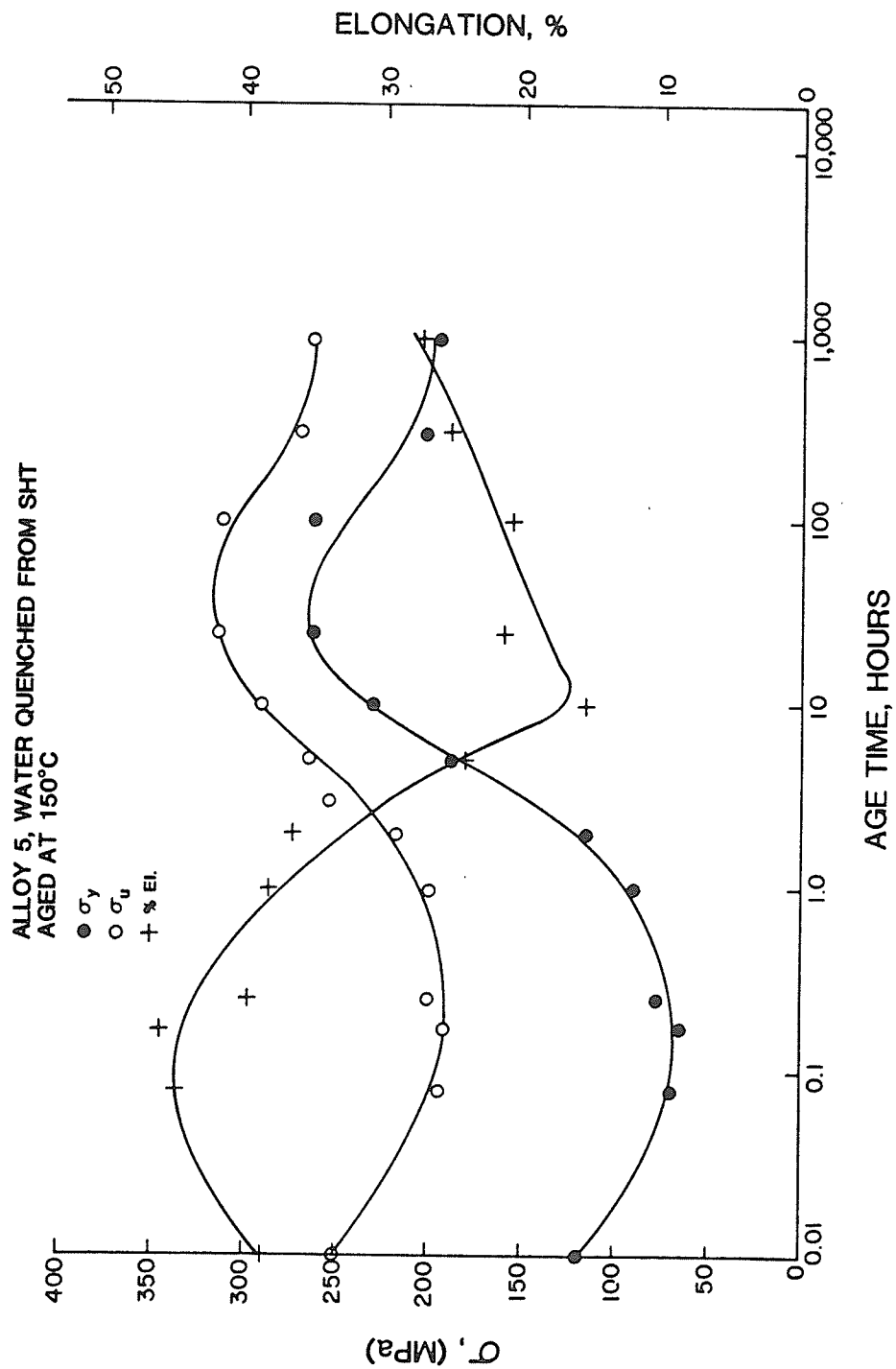


Figure 6. Effect of aging time on tensile properties of alloy 5 water quenched from SHT and aged at 423K [150°C].

TABLE 7

Effect of Aging Time at 423K [150°C] on Hardness of Alloys 4 and 5 Without Prior Natural Aging

HARDNESS (VPN), μ , AND STANDARD DEVIATION, σ			
HEAT TREATMENT		ALLOY 4	ALLOY 5
As Quenched	μ	45.5	48.6
	σ	0.9	1.5
5 min	μ	43.2	46.1
	σ	2.1	0.6
10 min	μ	42.8	45.7
	σ	0.6	0.3
15 min	μ	44.0	44.5
	σ	1.5	0.6
1 hour	μ	47.8	45.1
	σ	0.5	0.4
2 hours	μ	49.1	45.8
	σ	1.8	1.8
3 hours	μ	56.7	46.7
	σ	3.5	0.7

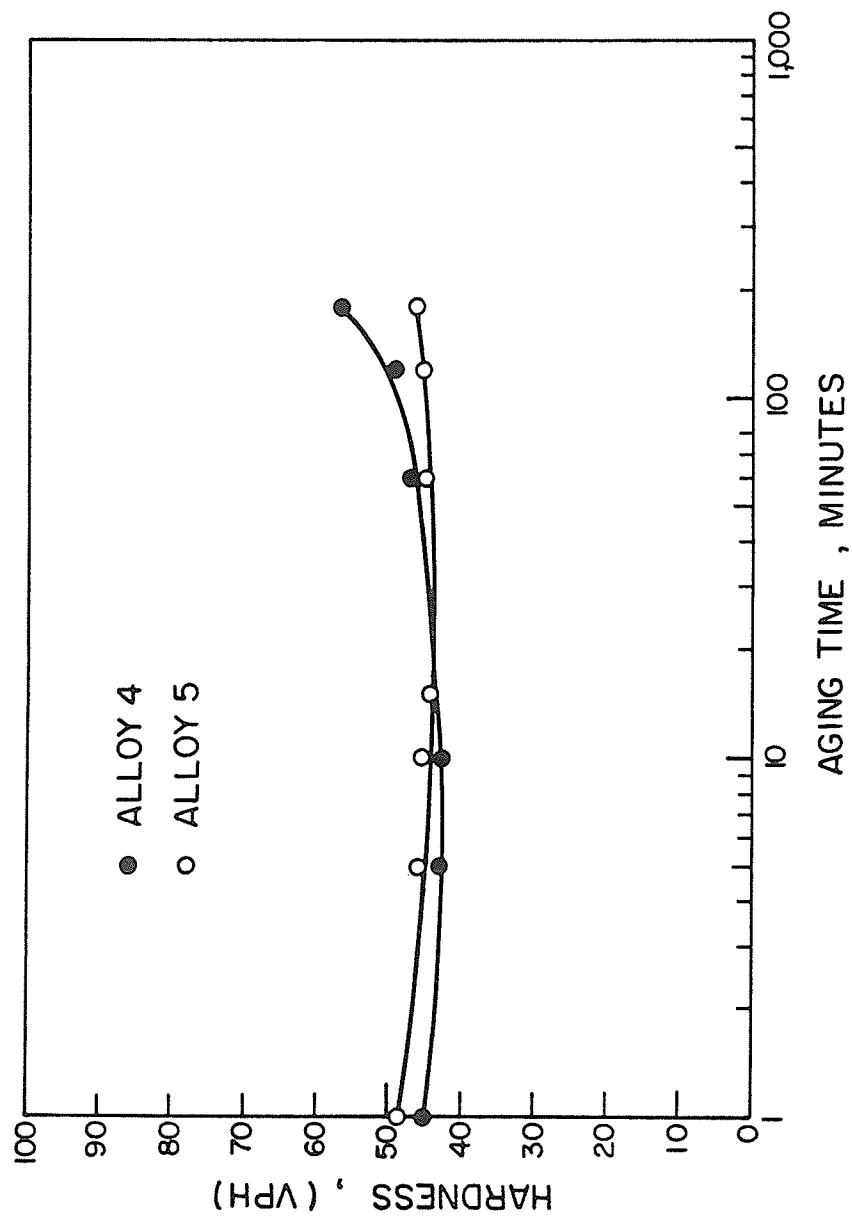


Figure 7. Effect of aging time on hardness of alloys 4 and 5 water quenched from SHT and aged at 423K [150°C] without prior room temperature aging.

The influence of natural aging prior to aging at 423K [150°C] on the tensile properties of both alloys is shown in Table 8 and Figures 8 and 9. The yield strength of alloy 4 increased from 51.5 MPa in the as-quenched condition to 133.3 MPa after 3 hours of aging, however, only a slight increase in the yield strength, 69.1 to 75.3 MPa, of alloy 5 was observed. The ultimate tensile strength of alloy 5 remained fairly constant on aging for up to 3 hours, whereas that of alloy 4 increased from 173.9 to 226.3 after 3 hours of aging. The elongation to fracture of alloy 4 decreased from 45.5 to 35.7%, however, that of alloy 5 remained fairly constant during 3 hours of aging at 423K [150°C].

4.1.2.2. Aging at 393K [120°C]

The influence of aging at 393K [120°C] on the hardness and tensile properties of alloys 4 and 5 was determined by solution heat treating specimens at 773K [500°C] for 30 minutes, water quenching to room temperature, holding at room temperature for 16 hours followed by artificial aging at 393K [120°C] for various lengths of time. It was observed that an initial decrease in hardness from 70 to about 50 VPN took place after approximately 10 minutes of aging as was the case when the alloys were aged at the higher temperature, 423K [150°C], reported in the previous section. However, the hardness of both alloys increased to a maximum of

TABLE 8

Tensile Properties of Alloys 4 and 5, Aged
at 423K[150°C] Without Prior Natural Aging

HEAT TREATMENT	ALLOY	σ_y (MPa)	σ_u (MPa)	%El
As Quenched	#4	51.5	173.9	45.5
	#5	69.1	194.6	43.1
5 minutes	#4	58.9	176.7	46.7
	#5	60.5	187.5	49.4
10 minutes	#4	62.0	179.8	45.8
	#5	79.6	189.8	45.3
15 minutes	#4	79.5	190.7	44.4
	#5	65.9	194.6	48.0
1 hour	#4	110.6	199.0	34.8
	#5	68.2	195.3	47.6
2 hours	#4	132.5	216.5	27.7
	#5	81.1	199.6	43.8
3 hours	#4	133.3	226.3	35.7
	#5	75.3	194.6	44.0

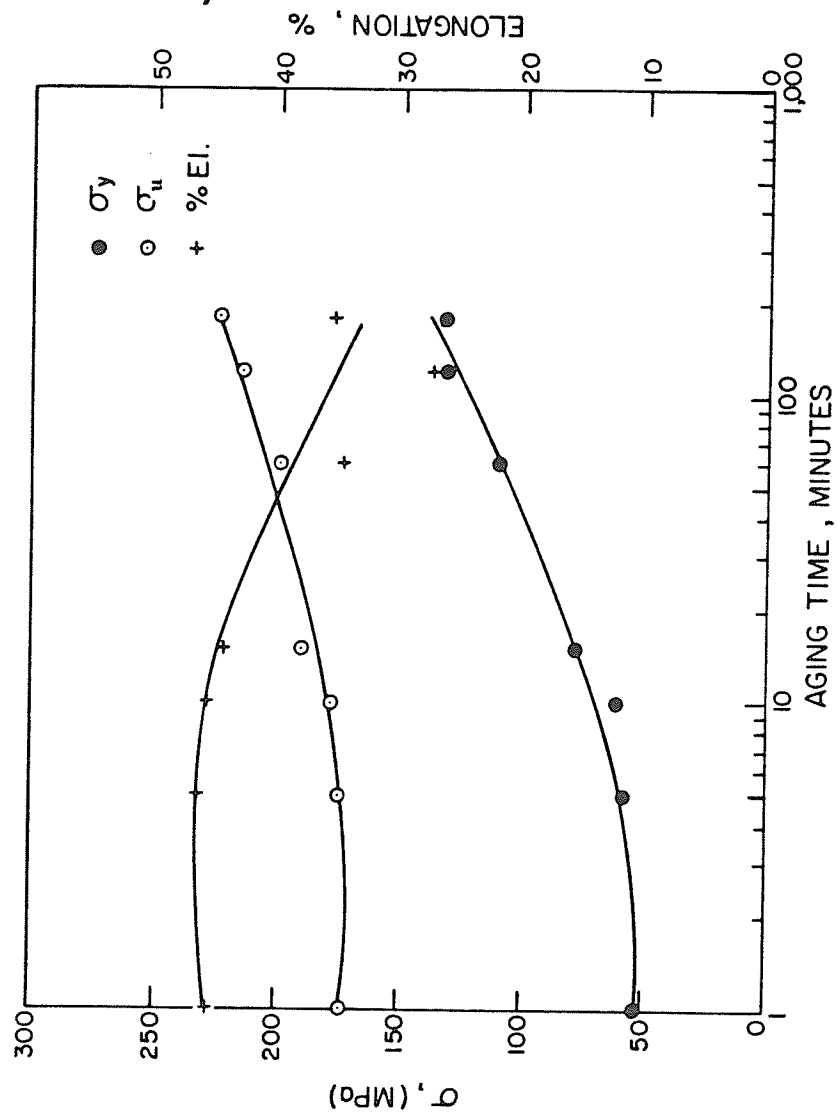


Figure 8. Effect of aging time on tensile properties of alloy 4 water quenched from SHT and aged at 423K [150°C] without prior room temperature aging.

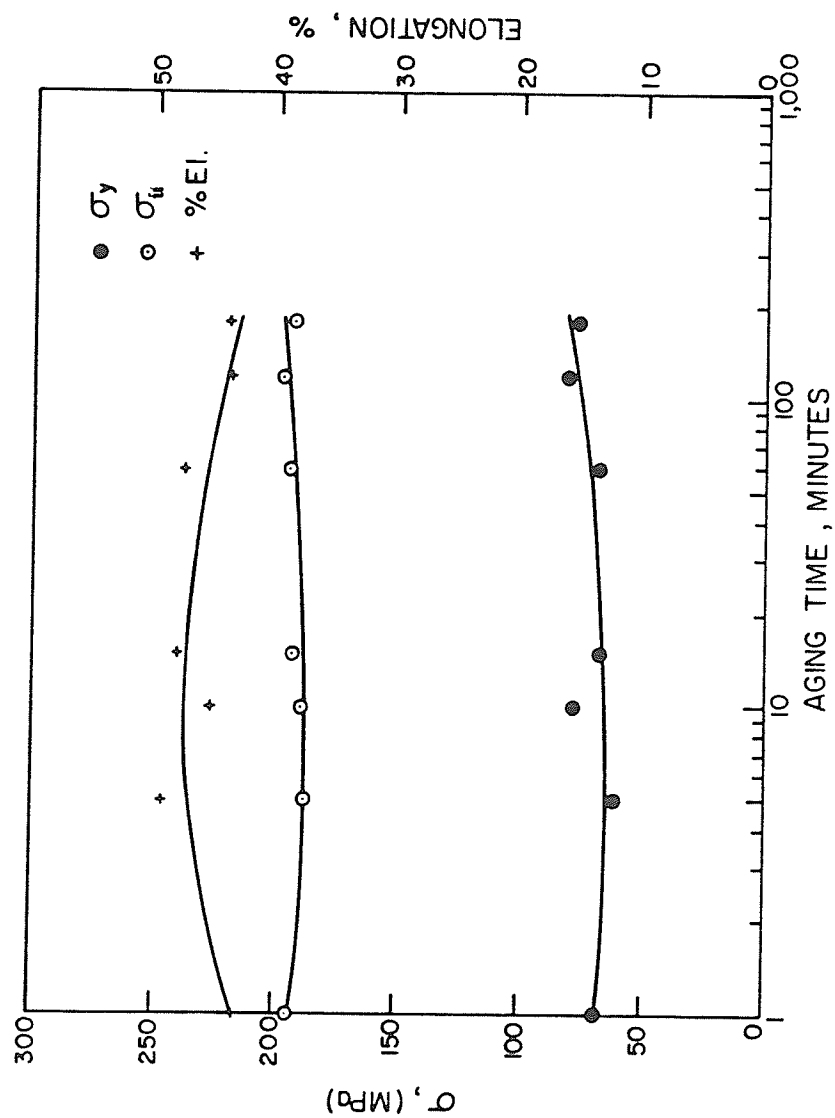


Figure 9. Effect of aging time on tensile properties of alloy 5 water quenched from SHT and aged at 423K [150°C] without prior room temperature aging.

135 VPN after aging for 300 hours at 393K [120°C], and then decreased to 125 VPN after 2000 hours, Table 5 and Figure 4.

A similar trend to that for hardness was observed for the yield and ultimate tensile strength of both alloys. When the zirconium free alloy, alloy 4, was aged at 393K [120°C] its yield strength decreased from 108.2 to 76 MPa after 10 minutes, then increased to 350 MPa after 300 hours and once again it decreased to 306 MPa after 2000 hours. Its ultimate tensile strength decreased from 237.3 to 196 MPa after 10 minutes of aging and then increased to 373.5 MPa after 300 hours. It decreased, however, to 344 MPa after 2000 hours of aging. The elongation to fracture of the same alloy increased from 39.3 to 41.5% after 10 minutes of aging at 393K [120°C], which was followed by a decrease to 13.2% after 300 hours. The elongation to fracture once again increased to 21.8% after 2000 hours, Table 9 and Figure 10.

The yield strength of the zirconium containing alloy, alloy 5, decreased from 118.1 to 73.5 MPa after aging at 393K [120°C] for 10 minutes and then increased to 348 MPa after 300 hours. This was followed by a decrease to 322 MPa after 2000 hours of aging. Its ultimate strength decreased from 250.8 to 202 MPa after 10 minutes and then increased to 356 MPa after 300 hours. However, it decreased only slightly on further aging for up to 2000 hours. The elongation to fracture increased from 38.6 to 44% after 10 minutes of aging

TABLE 9

Tensile Properties of Alloys 4 and 5
Aged at 393K[120°C]

HEAT TREATMENT	ALLOY	σ_y (MPa)	σ_u (MPa)	%El
As Quenched	#4	51.5	173.9	45.5
	#5	69.1	194.6	43.1
As Quenched +16h RT	#4	108.2	237.3	39.3
	#5	118.1	250.8	38.6
5 minutes	#4	86.0	224.5	40.0
	#5	95.0	225.0	40.0
10 minutes	#4	76.0	196.0	41.5
	#5	73.5	202.0	44.0
15 minutes	#4	73.0	197.0	41.5
	#5	75.0	201.0	45.0
1 hour	#4	83.0	201.0	40.5
	#5	79.5	205.0	42.0
2 hours	#4	113.6	224.1	36.9
	#5	99.2	213.9	45.0
3 hours	#4	129.4	237.2	34.7
	#5	119.0	226.0	38.0
5 hours	#4	147.9	246.5	33.7
	#5	124.0	229.5	38.0
10 hours	#4	163.2	251.1	26.5
	#5	173.0	250.0	25.0
24 hours	#4	229.4	294.5	24.5
	#5	205.0	279.0	30.0
100 hours	#4	310.0	345.5	17
	#5	326.0	342.5	23.1
300 hours	#4	350.0	373.5	13.2
	#5	348.0	356.0	19.2
600 hours	#4	345.0	371.0	10.5
	#5	341.0	356.0	19.8
1000 hours	#4	329.5	356.0	15.2
	#5	322.0	352.0	22.7
2000 hours	#4	306.0	344.0	21.8
	#5	322.0	354.5	22.0

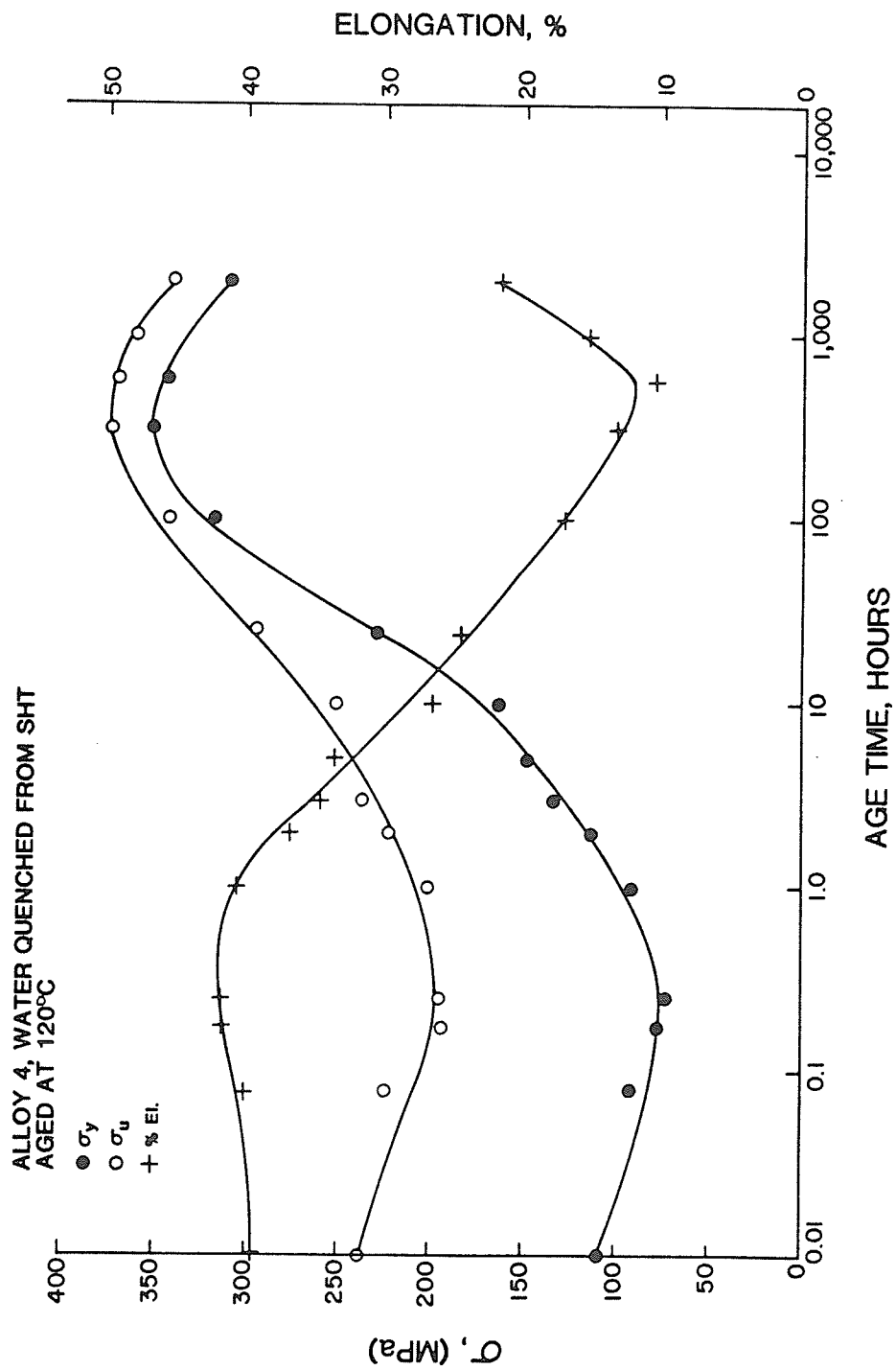


Figure 10. Effect of aging time on tensile properties of alloy 4 water quenched from SHT and aged at 393K[120°C].

and then decreased to 19.2% after 300 hours. It increased, however, to 22% after 2000 hours, as shown in Table 9 and Figure 11.

4.1.3. Microstructural Studies

The aging behaviour of both alloys was studied by optical as well as transmission electron microscopy. It was decided to examine samples after heat treatments for which the hardness and the strength curves contain areas of interest. As described earlier the hardness and strength of both alloys decreased after 10 minutes of aging at both 423K [150°C] and 393K [120°C]. This was followed by an increase to a maximum after 24 hours of aging at 423K [150°C] and 300 hours at 393K [120°C]. Overaging i.e. decrease in hardness and strength took place after 1000 hours at 423K [150°C] and 2000 hours at 393K [120°C].

4.1.3.1. Solution Heat Treated Material

The influence of zirconium additions on the microstructure of 7004 aluminum-zinc-magnesium alloy was determined by examining the two alloys under the optical microscope. It was observed that the microstructure of the zirconium containing alloy, alloy 5, consisted of non-recrystallized grains, whereas that of the zirconium free alloy, alloy 4,

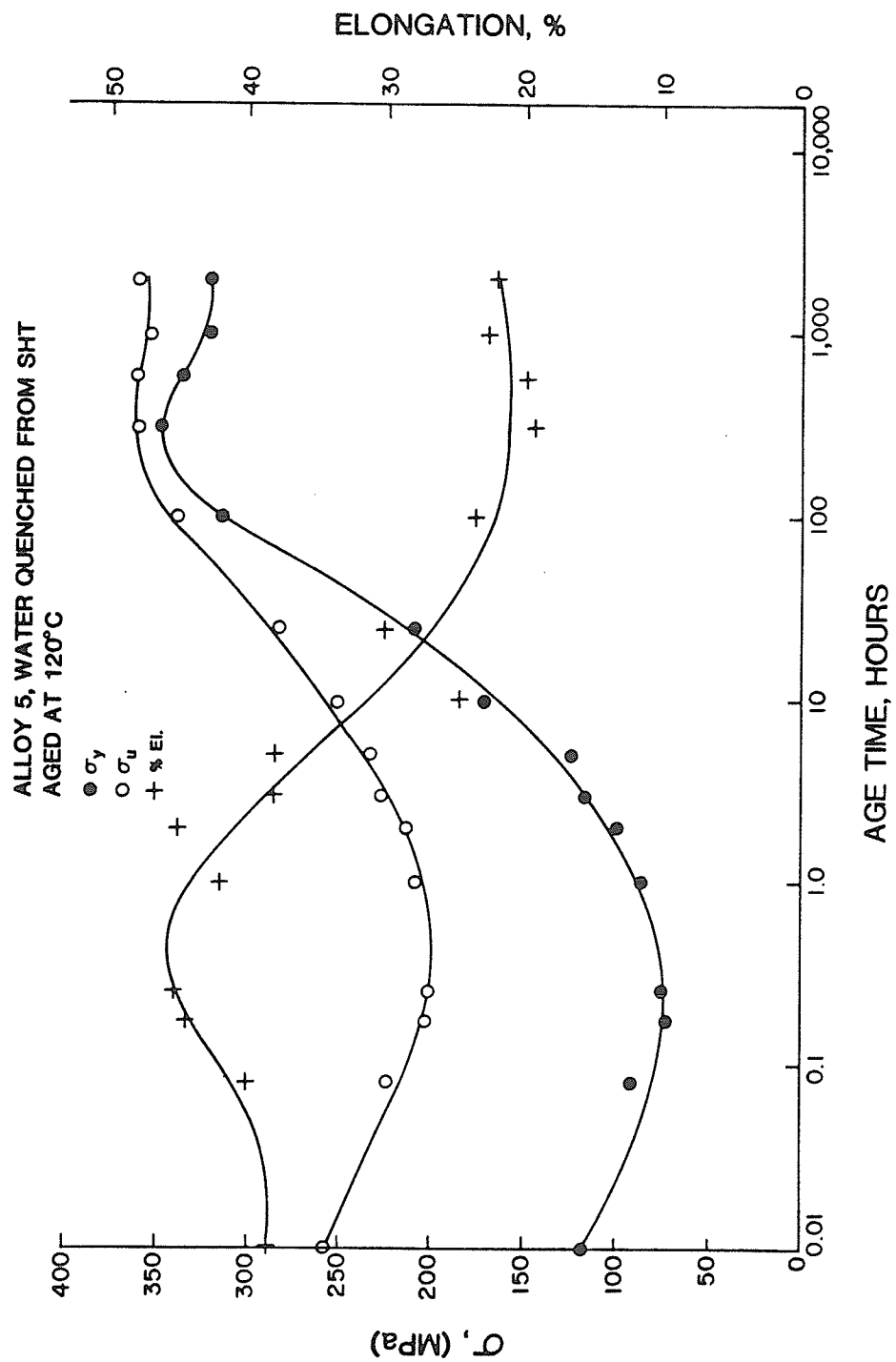


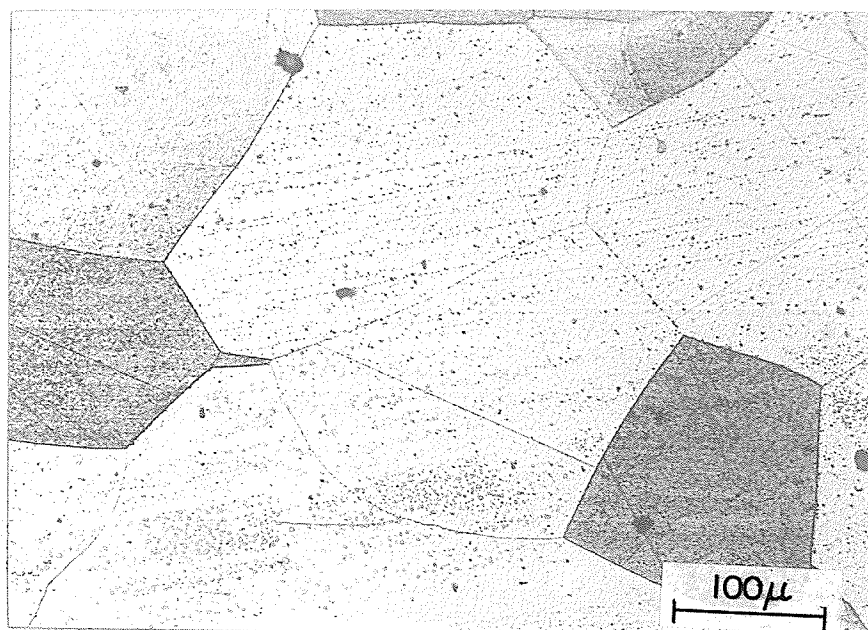
Figure 11. Effect of aging time on tensile properties of alloy 5 water quenched from SHT and aged at 393K[120°C].

consisted of large fully recrystallized grains as shown in Figure 12. Although optical microscopy did not reveal any differences in the variously cooled alloys from solution heat treatment temperature, thin foil observations showed that the cooling rate had a small effect on the microstructure of the solution heat treated and naturally aged alloys. After natural aging grain boundaries free from precipitate particles and precipitate free grains were observed in the water quenched samples. However, a small number of particles were observed within the grains of air cooled and block air cooled alloys, Figures 13 to 15.

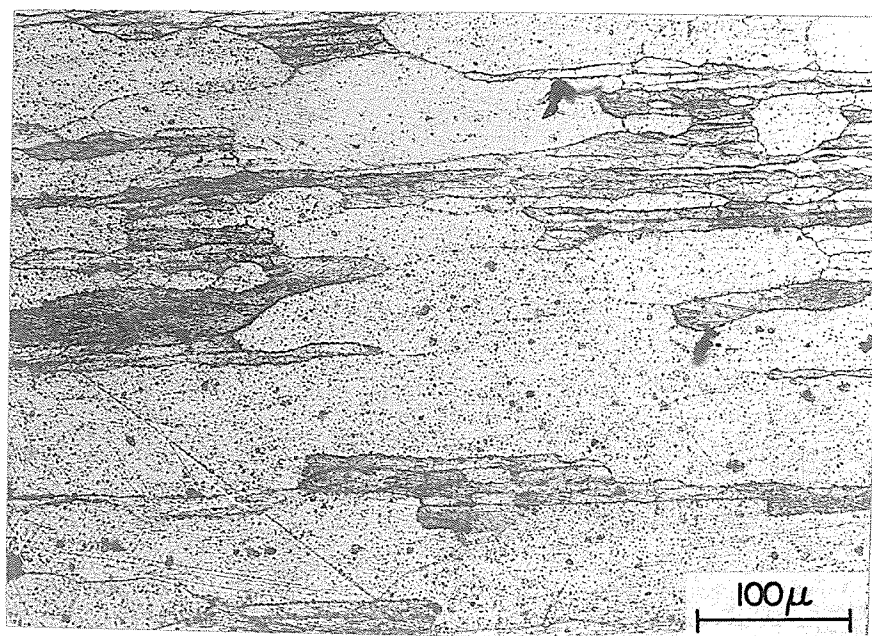
4.1.3.2. Aging at 423K [150°C]

Thin foils were made from samples aged for 10 minutes, 24 and 1000 hours at 423K [150°C] and examined in the transmission electron microscope in order to relate the microstructure produced after each heat treatment with hardness and tensile properties.

It was observed that after 10 minutes of aging the grain boundaries of the water quenched samples remained precipitate free, Figure 16. However, grain boundary particles had formed in air cooled and slowly cooled samples, Figures 17 and 18.

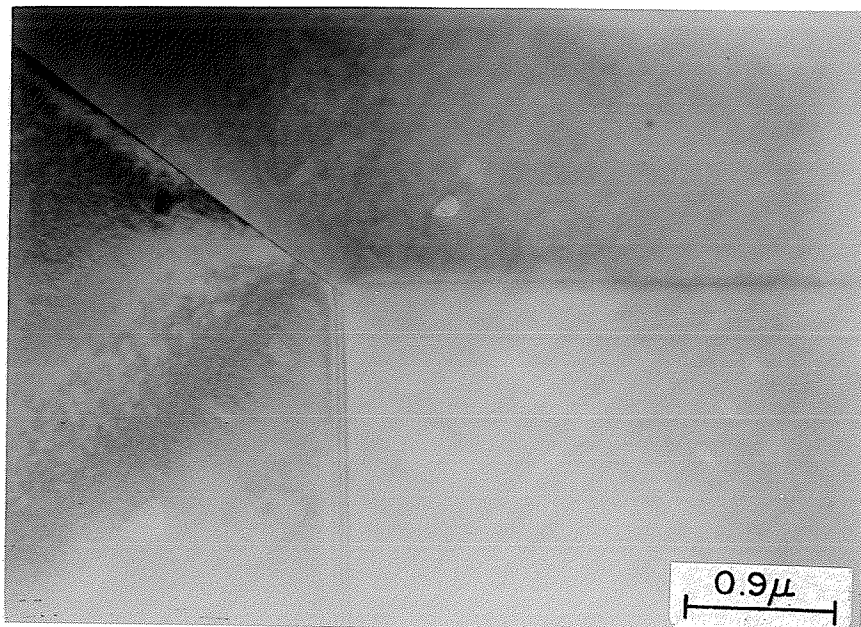


Alloy 4

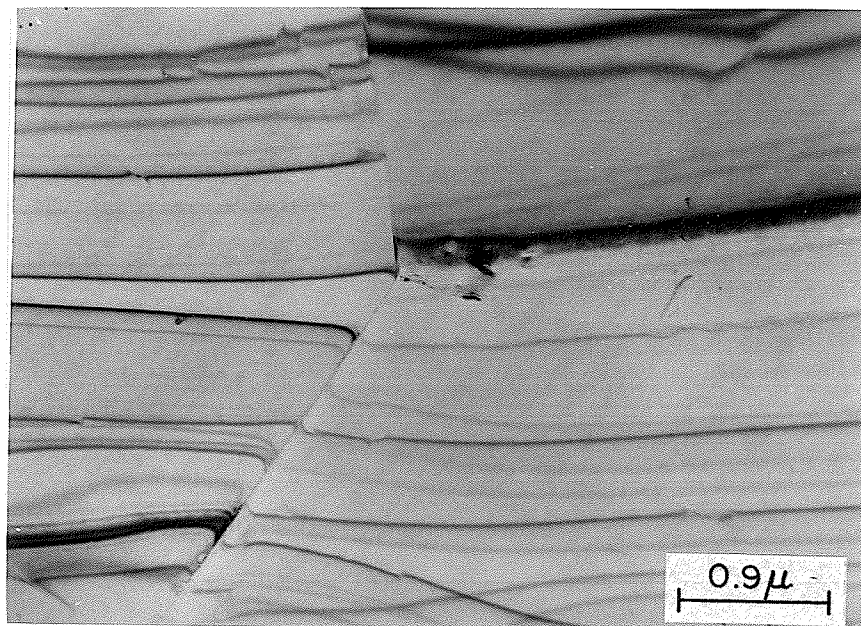


Alloy 5

Figure 12. Optical photomicrographs of alloys 4 and 5.

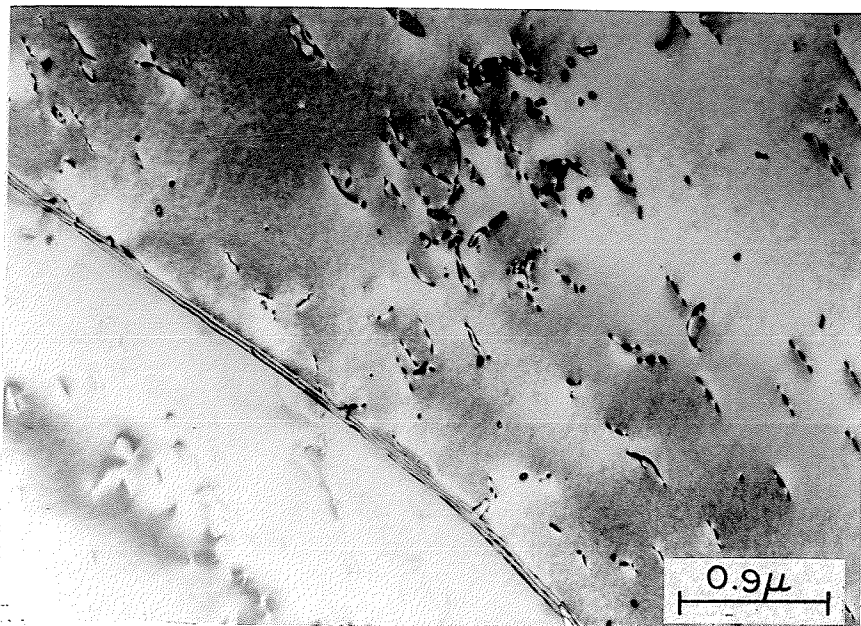


Alloy 4

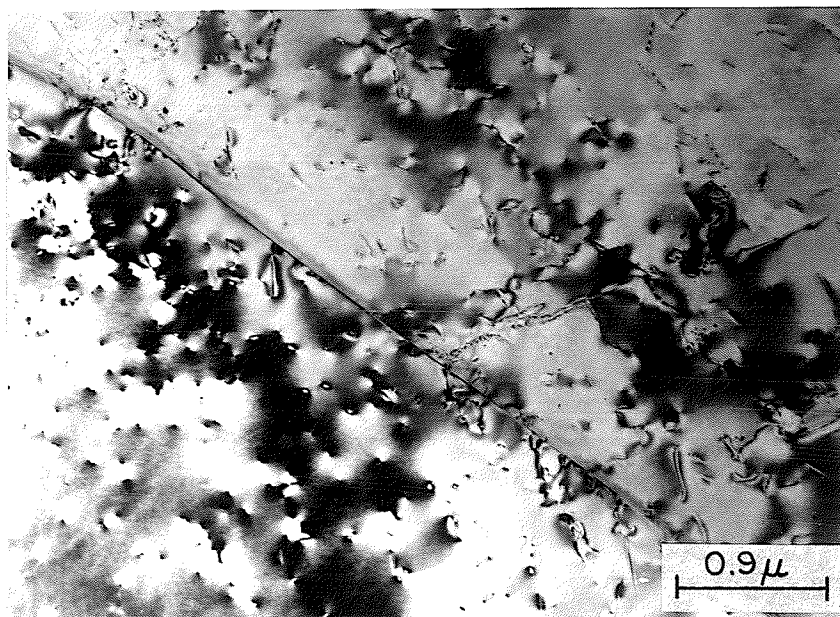


Alloy 5

Figure 13. TEM photomicrographs of alloys 4 and 5 water quenched from SHT and naturally aged for 16 hours.

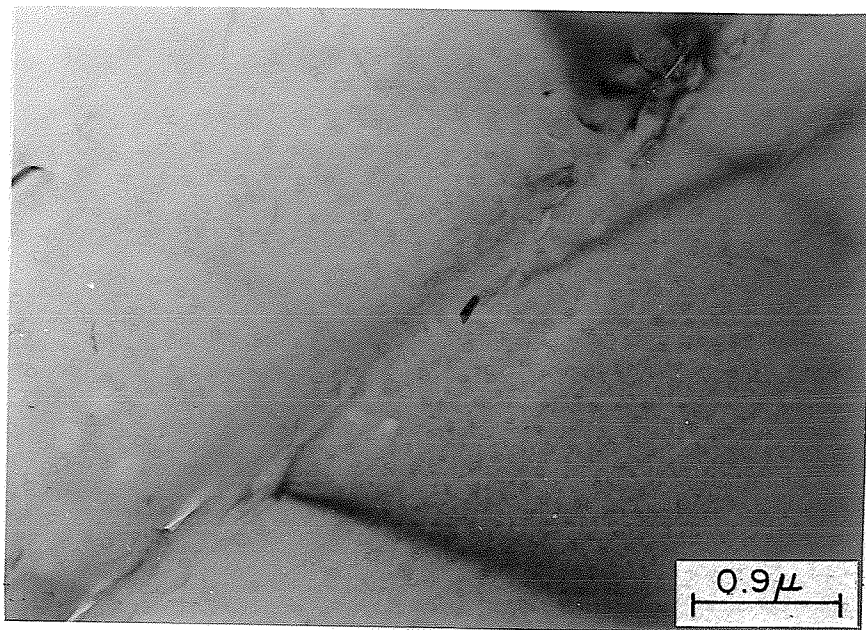


Alloy 4

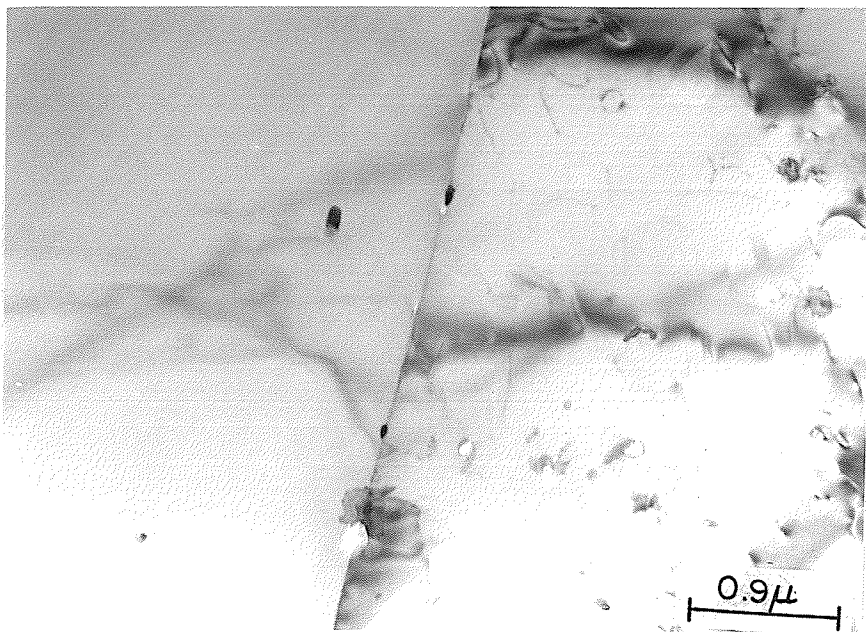


Alloy 5

Figure 14. TEM photomicrographs of alloys 4 and 5 air cooled from SHT and naturally aged for 16 hours.

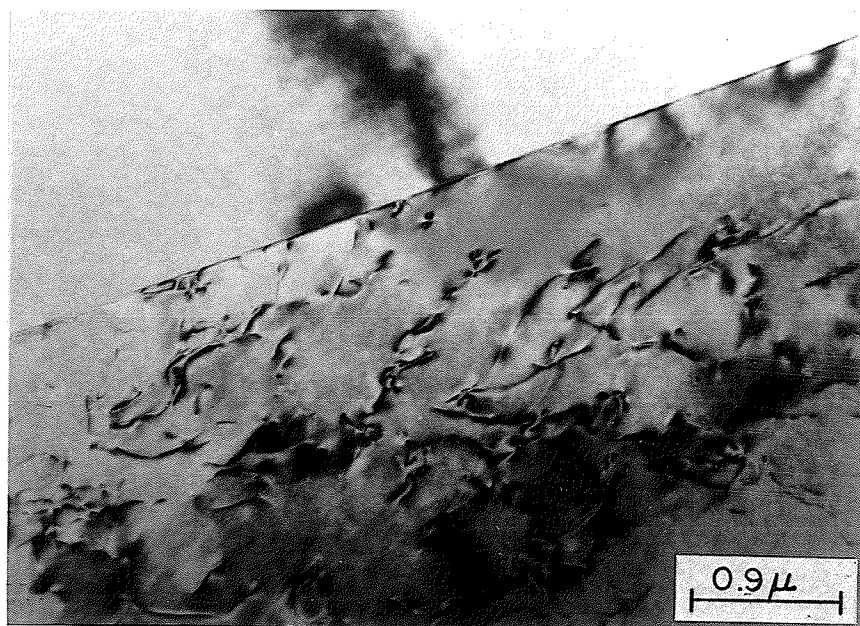


Alloy 4

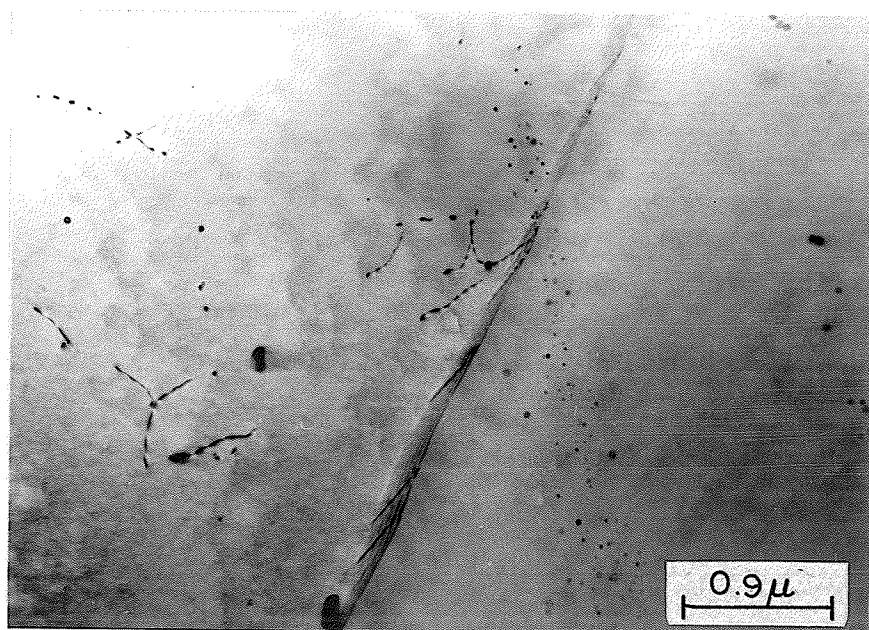


Alloy 5

Figure 15. TEM photomicrographs of alloys 4 and 5 block cooled from SHT and naturally aged for 16 hours.

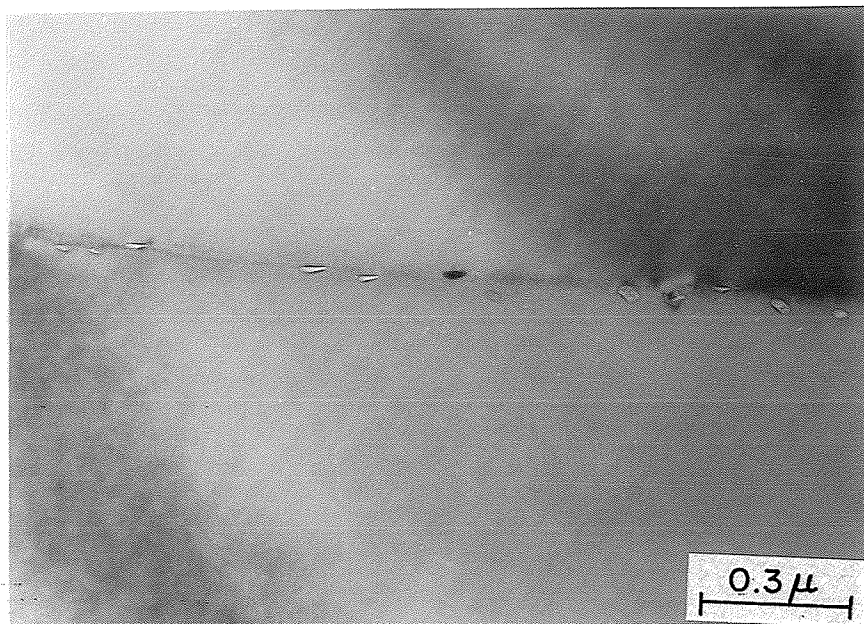


Alloy 4

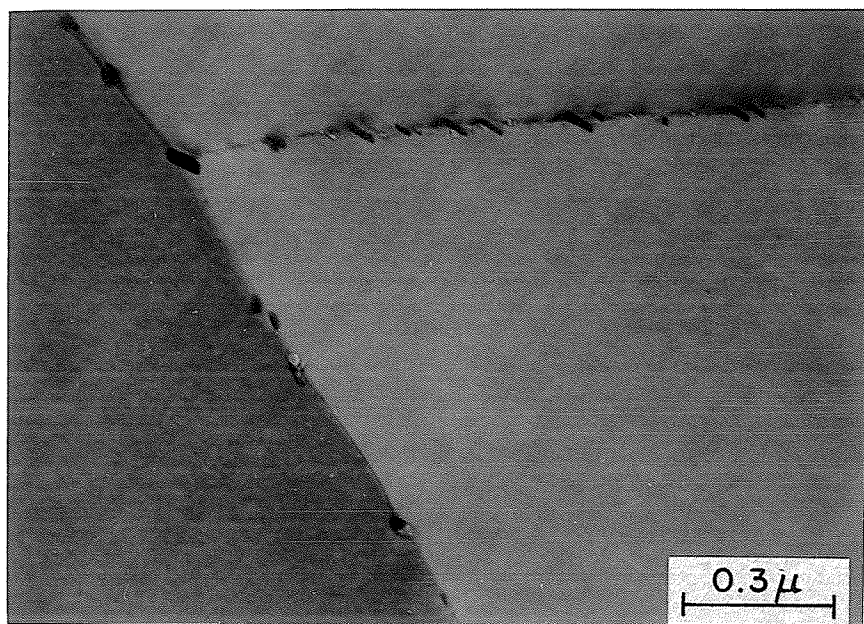


Alloy 5

Figure 16. TEM photomicrographs of alloys 4 and 5 water quenched from SHT, naturally aged for 16 hours and aged at 423K [150°C] for 10 minutes.

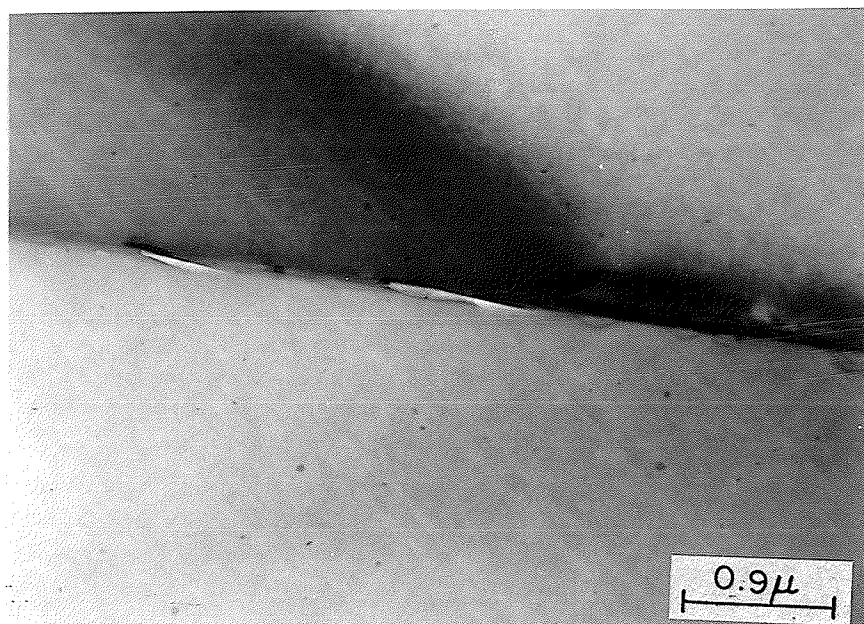


Alloy 4

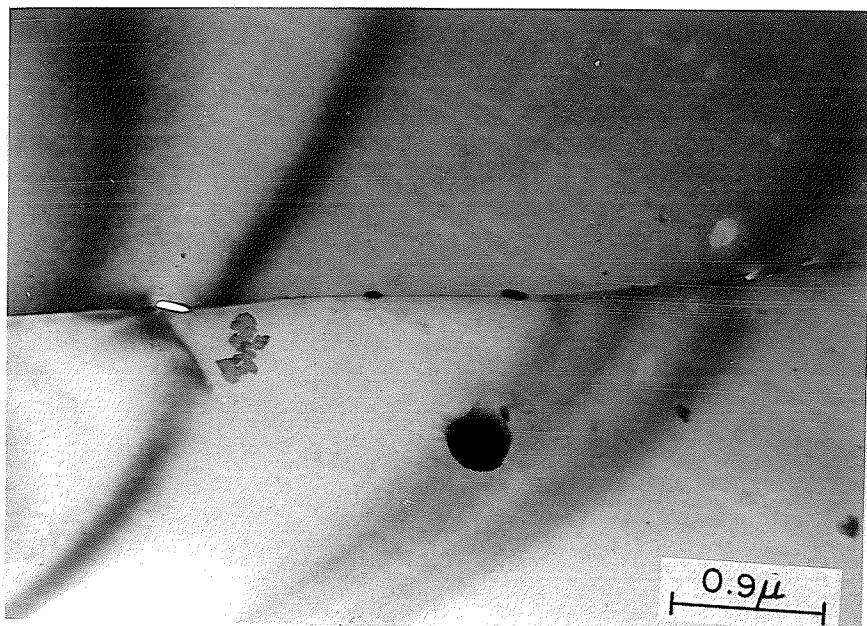


Alloy 5

Figure 17. TEM photomicrographs of alloys 4 and 5 air cooled from SHT, naturally aged for 16 hours and aged at 423K [150°C] for 10 minutes.



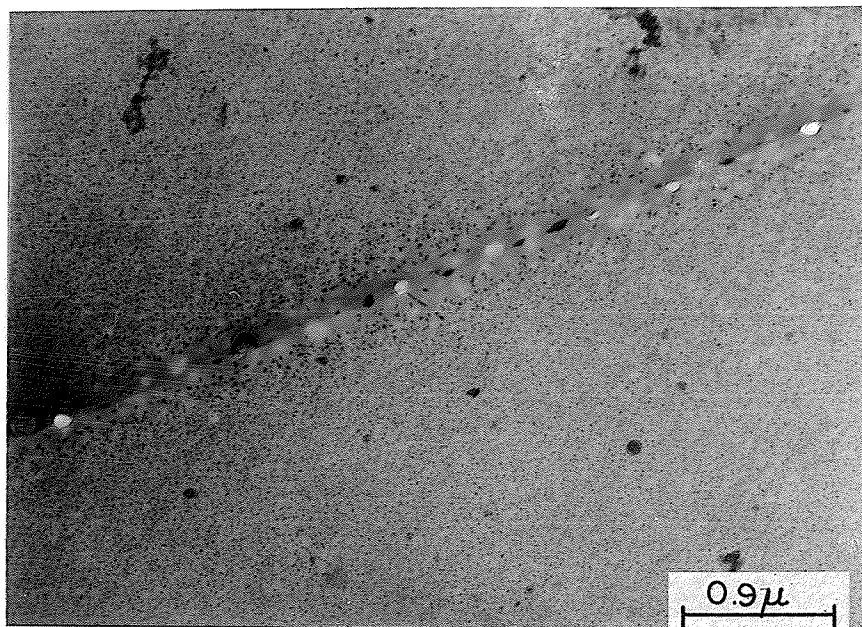
Alloy 4



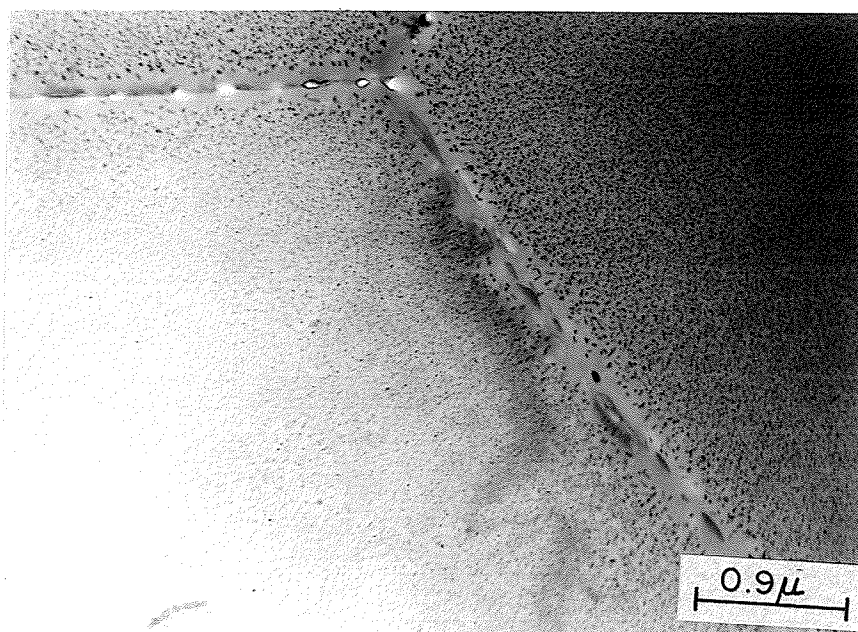
Alloy 5

Figure 18. TEM photomicrographs of alloys 4 and 5 block cooled from SHT, naturally aged for 16 hours and aged at 423K [150°C] for 10 minutes.

On further aging for 24 hours $\text{MgZn}_2 \eta'$ particles have formed in the matrix of all samples and grain boundary precipitates have formed in the water quenched samples, Figure 19. Also, the grain boundary particles of air cooled and slowly cooled alloys, which formed at early stages of aging, have grown in size, as shown in Figures 20 and 21. Identification of matrix as well as grain boundary second phase particles was performed with the aid of electron diffraction analysis. Figure 22 shows a bright field micrograph of alloy 4 water quenched from solution heat treatment, naturally aged for 16 hours followed by artificial aging at 423K [150°C] for 24 hours where a maximum in the aging curve was observed. The foil has been tilted and as a result the grain boundary is not parallel to the electron beam. This was done in order to enhance the precipitate reflections. The selected area diffraction pattern of Figure 22 is shown in Figure 23 along with identification of the major matrix and precipitate reflections. Matrix precipitates $\text{MgZn}_2 \eta'$ are shown in the dark field micrograph, Figure 24, taken using the (2022) η' reflection, whereas grain boundary precipitates $\text{MgZn}_2 \eta$ are shown in the dark field micrograph, Figure 25, taken using the (0002) MgZn_2 reflection. Also, clearly distinguishable precipitate free zones, which start forming in the early stages of precipitate formation, were observed in all samples that were aged for 24 hours.

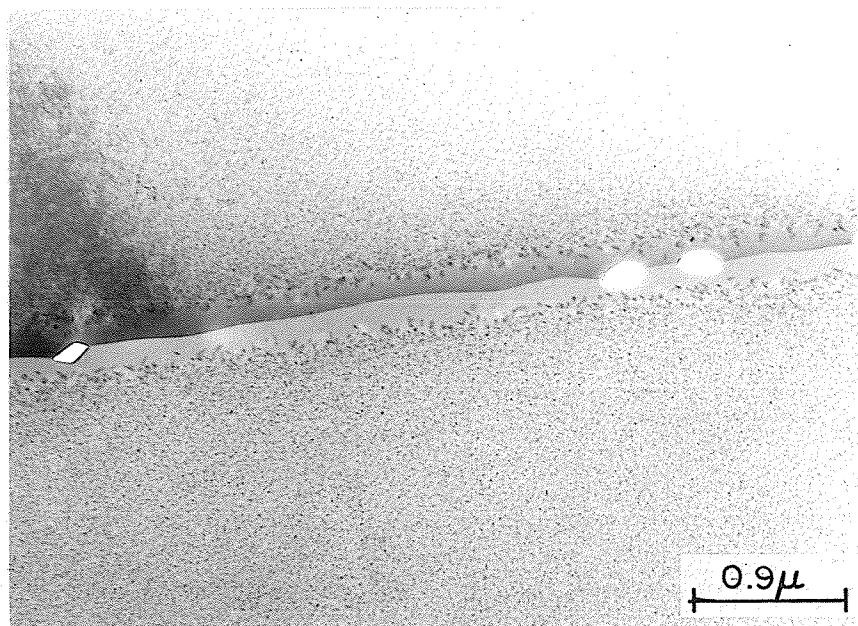


Alloy 4

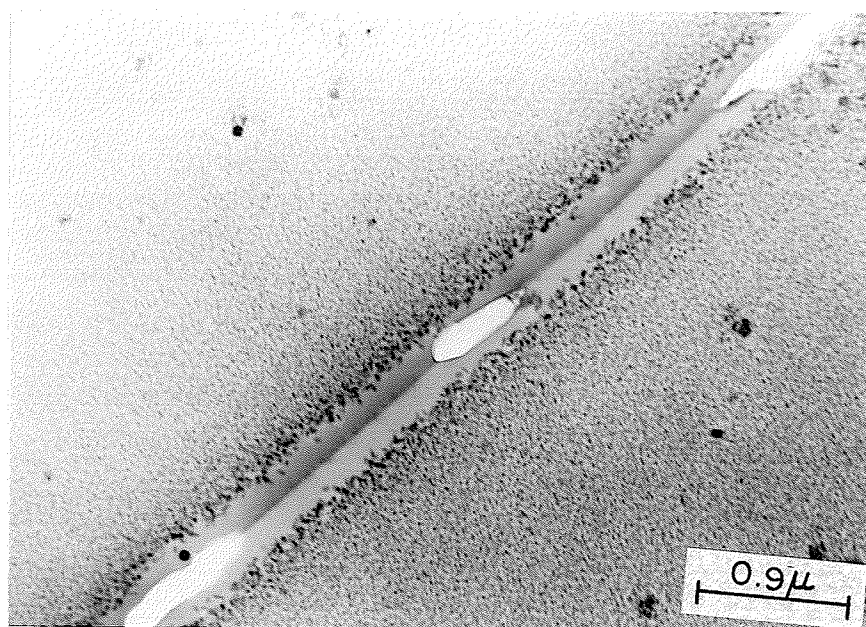


Alloy 5

Figure 19. TEM photomicrographs of alloys 4 and 5 water quenched from SHT, naturally aged for 16 hours and aged at 423K [150°C] for 24 hours.

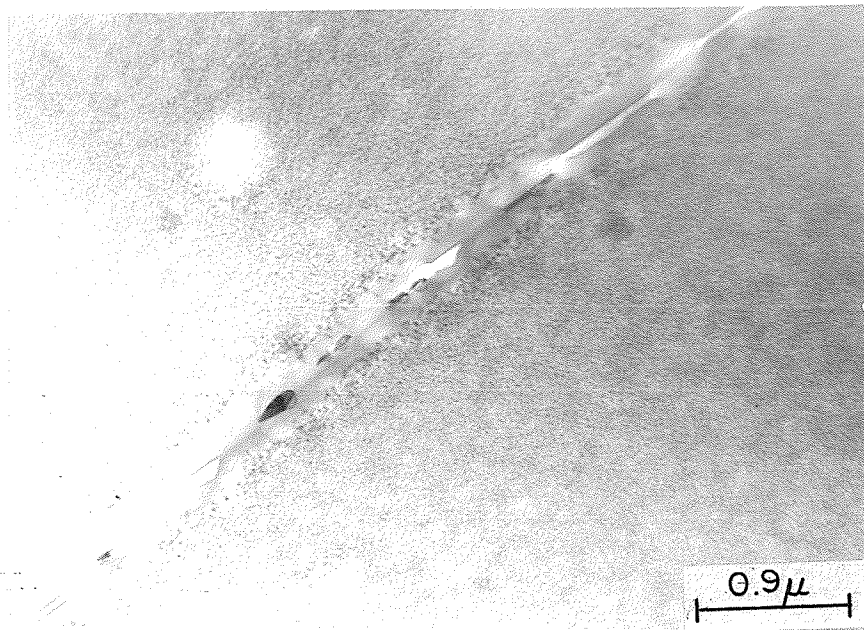


Alloy 4

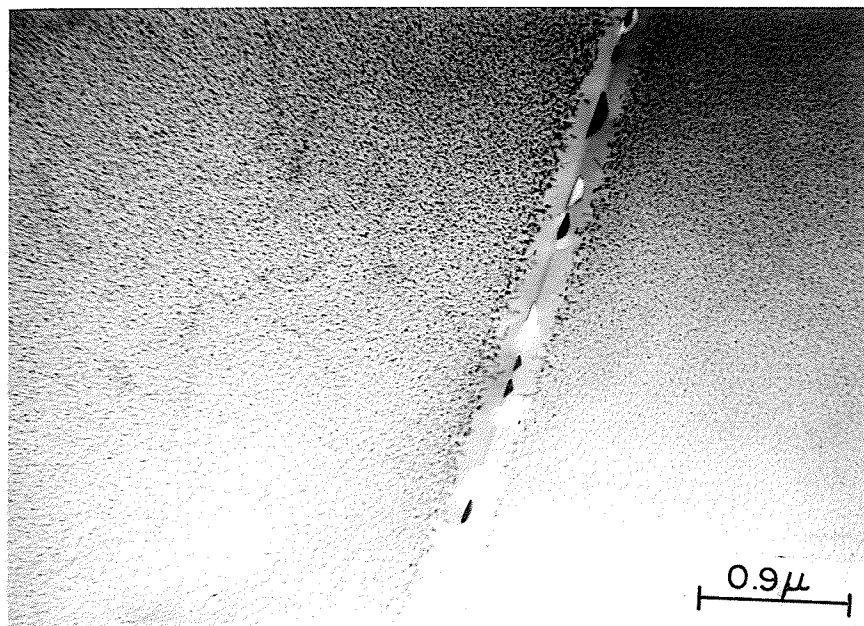


Alloy 5

Figure 20. TEM photomicrographs of alloys 4 and 5 air cooled from SHT, naturally aged for 16 hours and aged at 423K [150°C] for 24 hours.



Alloy 4



Alloy 5

Figure 21. TEM photomicrographs of alloys 4 and 5 block cooled from SHT, naturally aged for 16 hours and aged at 423K [150°C] for 24 hours.

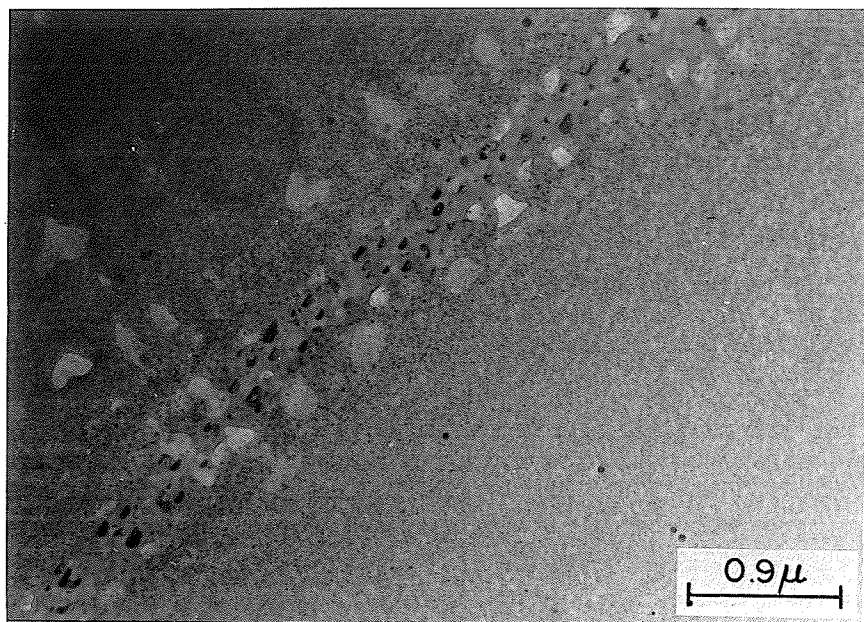


Figure 22. TEM photomicrograph of alloy 4, water quenched from SHT, naturally aged for 16 hours and aged at 423K [150°C] for 24 hours.

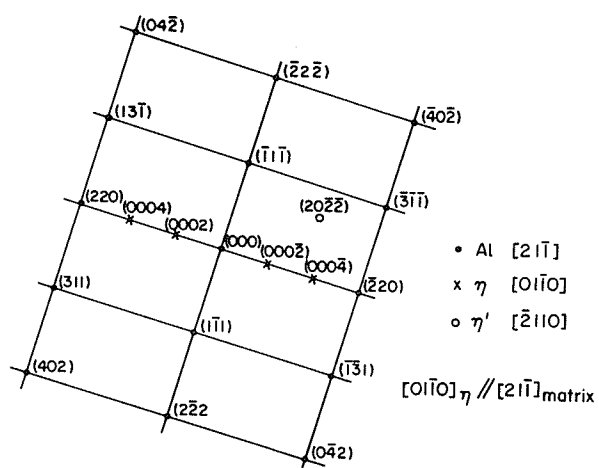


Figure 23. Selected area diffraction pattern of photomicrograph shown in Figure 22.

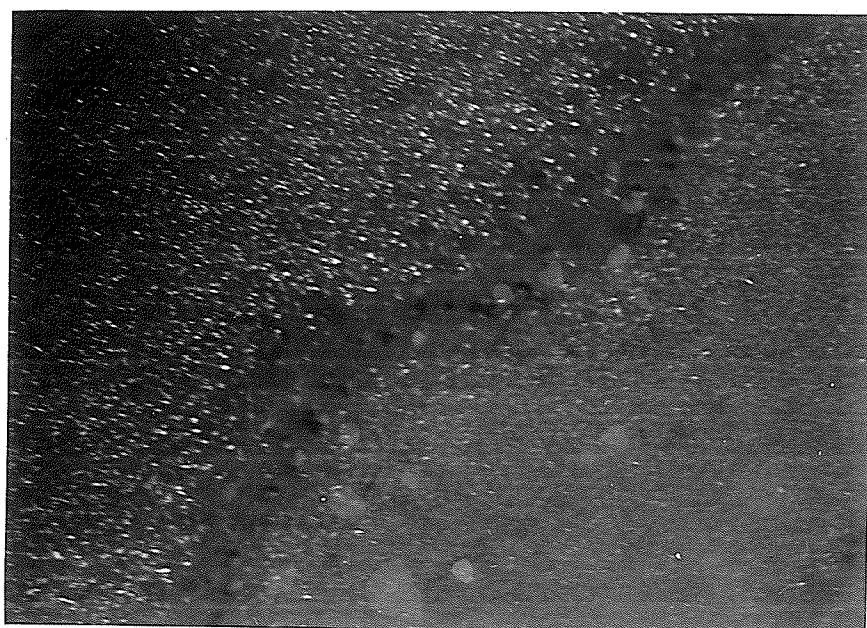


Figure 24. SADP and dark field from Figure 22 showing η'
 MgZn_2 .

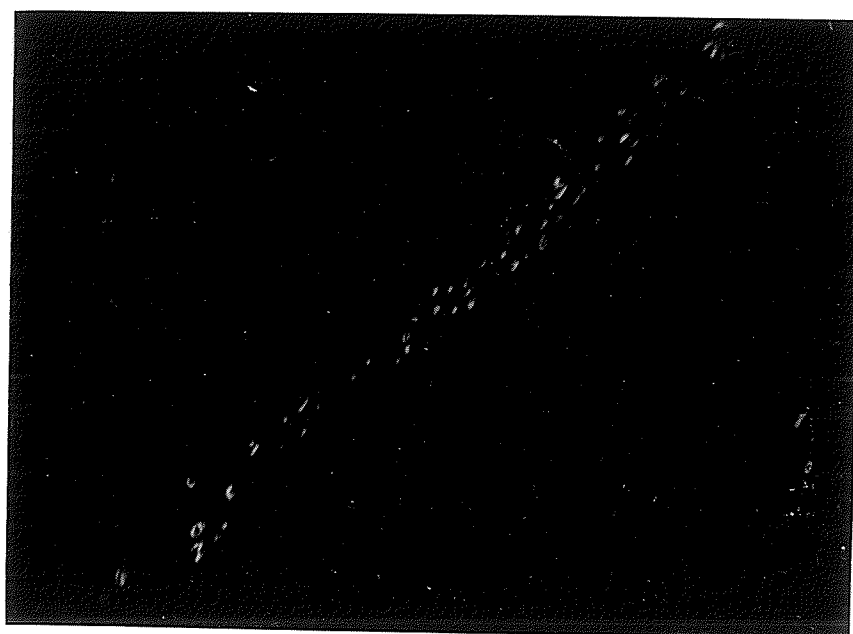


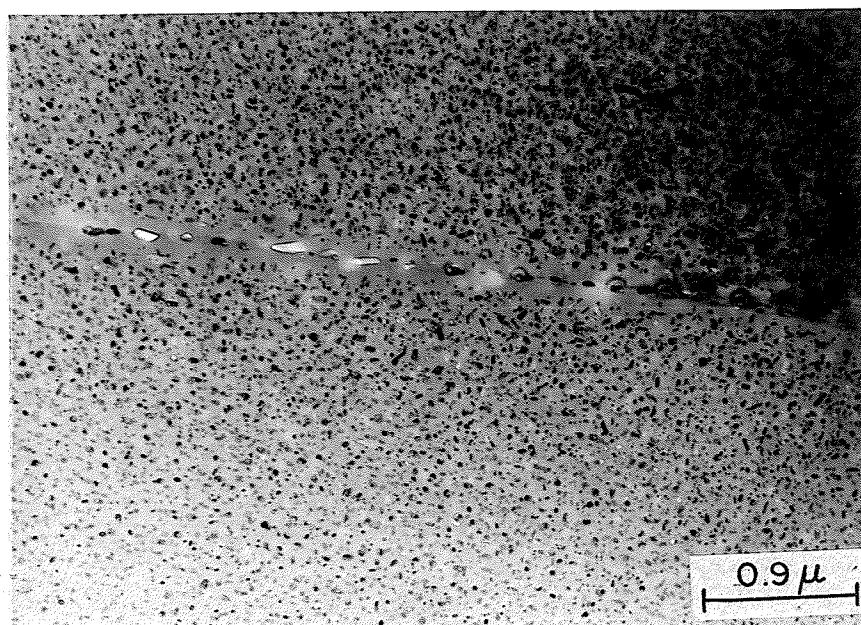
Figure 25. SADP and dark field from Figure 22 showing η
MgZn₂.

After 1000 hours of aging it was observed that in general the size of all precipitate particles had increased (Table 10) and MgZn_2 η particles of the platelet type had formed in the matrix. However, the width of the precipitate free zones was unaffected by aging time, Figures 26 - 28, Table 10.

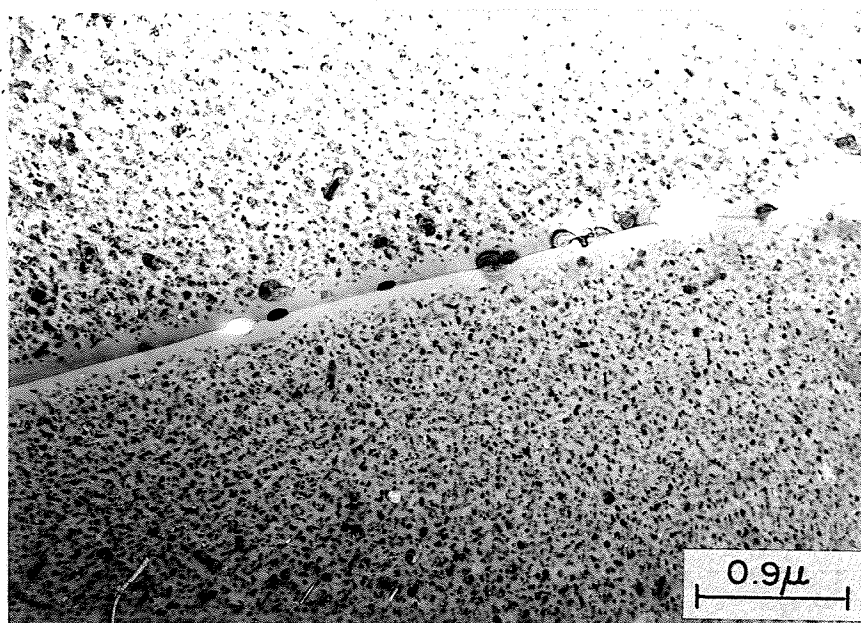
It was also observed that as the cooling rate from solution heat treatment decreased, the width of the precipitate free zones increased. The average width of the precipitate free zones in the specimens of alloy 4 increased from $(17.6 \pm 0.6) \times 10^2 \text{\AA}$ for water quenched samples to $(18.4 \pm 1.1) \times 10^2 \text{\AA}$ for air cooled and to $(23.4 \pm 2.2) \times 10^2 \text{\AA}$ for air cooled in a block followed by aging for 24 hours at 423K [150°C]. After the same heat treatment the width of the precipitate free zones in specimens of alloy 5 increased from $(16.0 \pm 0.8) \times 10^2$ observed in water quenched specimens to $(23.9 \pm 2.1) \times 10^2 \text{\AA}$ in air cooled and to $(45.0 \pm 4.2) \times 10^2 \text{\AA}$ for air cooled in block, as illustrated Table 10.

4.1.3.3. Aging at 393K [120°C]

In order to relate the microstructure produced upon aging of the alloys at 393K [120°C] with hardness and tensile properties, thin foils were also made from specimens aged for 10 minutes, 300 and 2000 hours and examined in the transmission electron microscope.

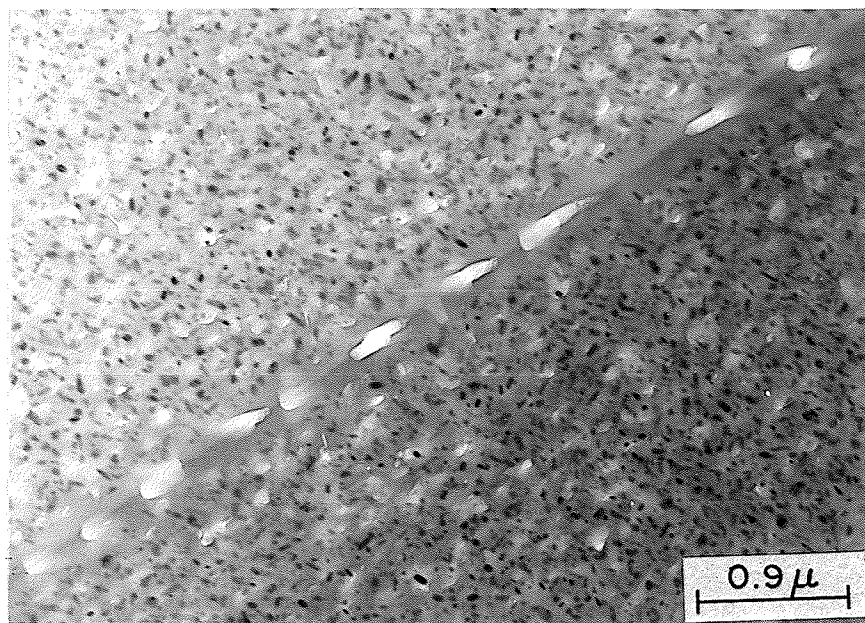


Alloy 4

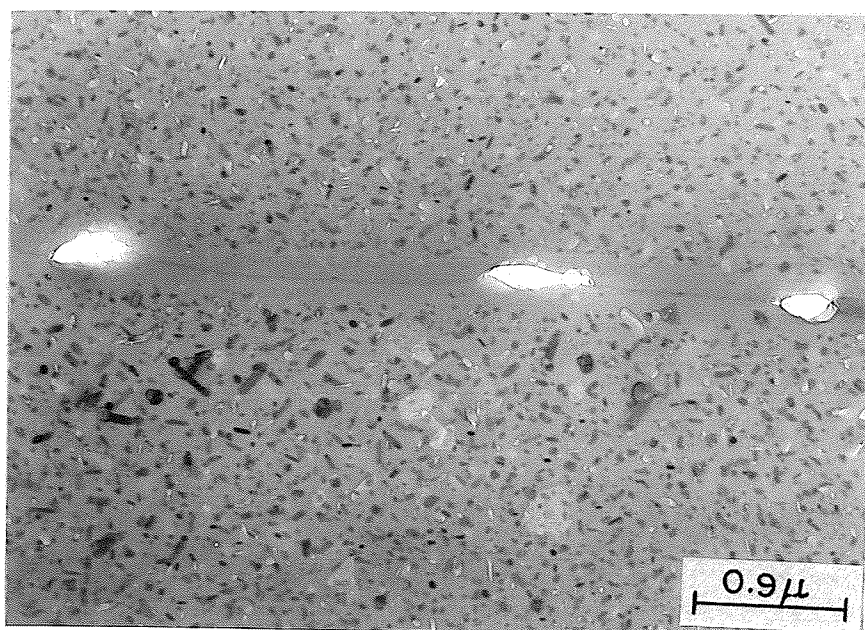


Alloy 5

Figure 26. TEM photomicrographs of alloys 4 and 5 water quenched from SHT, naturally aged for 16 hours and aged at 423K [150°C] for 1000 hours.

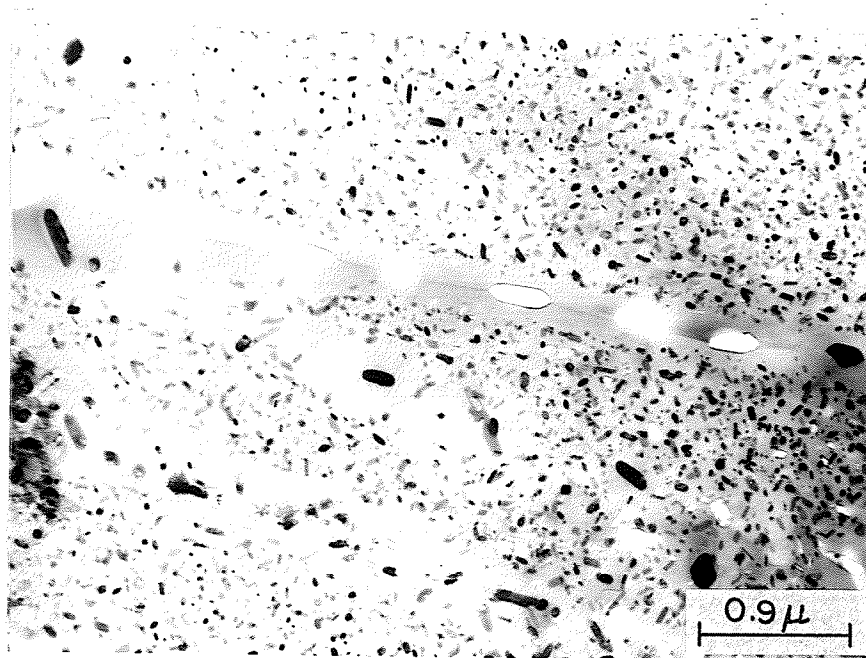


Alloy 4



Alloy 5

Figure 27. TEM photomicrographs of alloys 4 and 5 air cooled from SHT, naturally aged for 16 hours and aged at 423K [150°C] for 1000 hours.



Alloy 5

Figure 28. TEM photomicrograph of alloy 5 block cooled from SHT, naturally aged for 16 hours and aged at 423K [150°C] for 1000 hours.

TABLE 10

(a) Grain Boundary Precipitate Size of Alloys 4 and 5, Naturally Aged for 16 hours and Artificially Aged at 423K[150°C]

Alloy	Age Time	Grain Boundary Precipitate Long Axis ($\times 10^2 \text{\AA}$)		
		Water Quenched	Air Cooled	Block Cooled
4	24 hours	8.9 $\pm$ 1.1	13.1 $\pm$ 2.3	24.4 $\pm$ 5.6
5	24 hours	9.1 $\pm$ 2.4	52.1 $\pm$ 19.7	31.8 $\pm$ 5.8
4	1000 hours	12.8 $\pm$ 2.1	23.4 $\pm$ 5.4	—
5	1000 hours	12.5 $\pm$ 3.5	37.1 $\pm$ 11.1	12.0 $\pm$ 2.5

(b) Precipitate Free Zone Width of Alloys 4 and 5, Naturally Aged for 16 Hours and Artificially Aged at 423[150°C]

Alloy	Age Time	Precipitate Free Zone Width ($\times 10^2 \text{\AA}$)		
		Water Quenched	Air Cooled	Block Cooled
4	24 hours	17.6 $\pm$ 0.6	18.4 $\pm$ 1.1	23.4 $\pm$ 2.2
5	24 hours	16.0 $\pm$ 0.8	23.9 $\pm$ 2.1	45.0 $\pm$ 4.2
4	1000 hours	14.6 $\pm$ 1.0	21.9 $\pm$ 1.4	—
5	1000 hours	14.5 $\pm$ 1.2	24.9 $\pm$ 3.3	17.2 $\pm$ 0.9

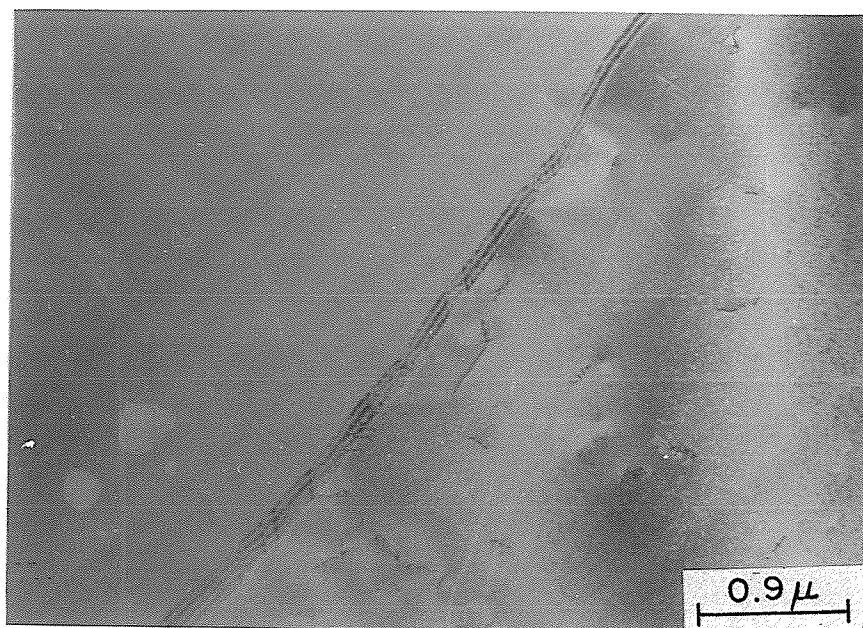
After 10 minutes of aging it was observed that the grain boundaries as well as the grain interiors of both alloys were free from precipitate particles (Figure 29).

Upon further aging for 300 hours, at which time peak hardness occurs, MgZn_2 η' particles were observed in the matrix of both alloys and grain boundary precipitates as well as precipitate free zones have formed (Figure 30).

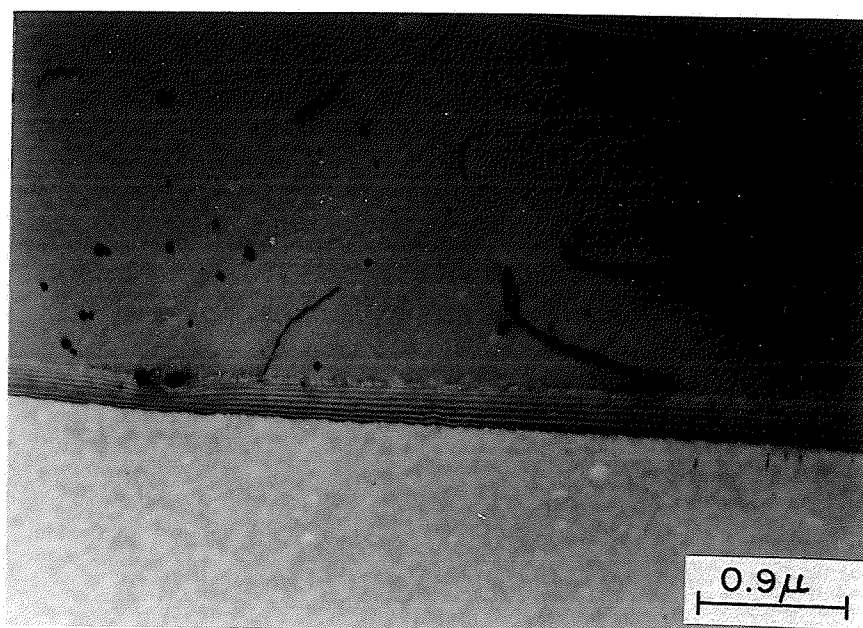
After 2000 hours of aging at 393K [120°C] the size of both grain boundary precipitates and matrix precipitates increased. However, the width of the precipitate free zones was not influenced by aging time at this temperature, as shown in Figure 31.

4.1.3.4. Differential Scanning Calorimetry

As mentioned earlier, no microstructural features which could be related to the initial drop in hardness and strength after 10 minutes of aging were observed upon TEM examination of thin foils. It was, therefore, decided to investigate the influence of natural aging on the initial stages of precipitation during artificial aging. This was done by determining the heat flow upon heating as a function of temperature using differential calorimetry experiments. It was observed that when the zirconium-containing alloy was aged at room temperature for 16 hours following water

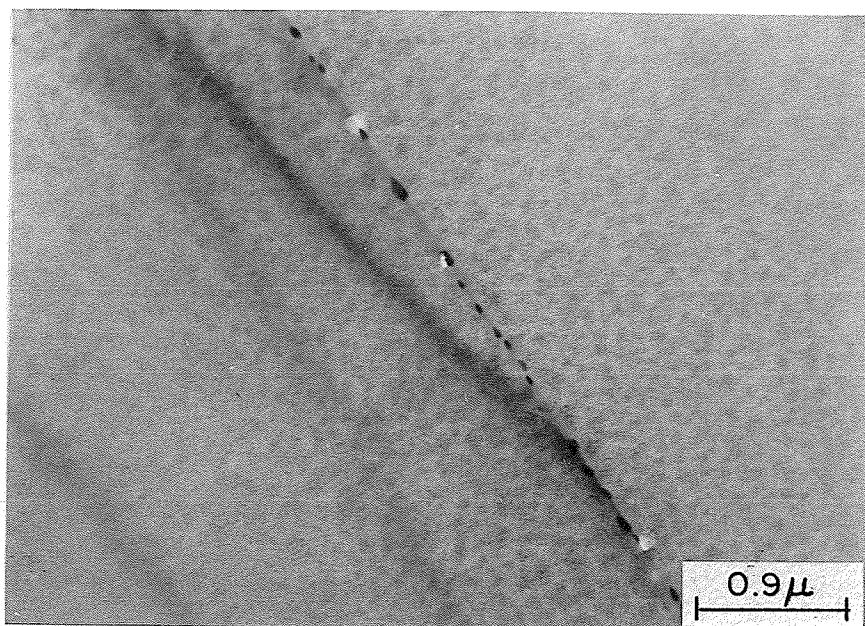


Alloy 4

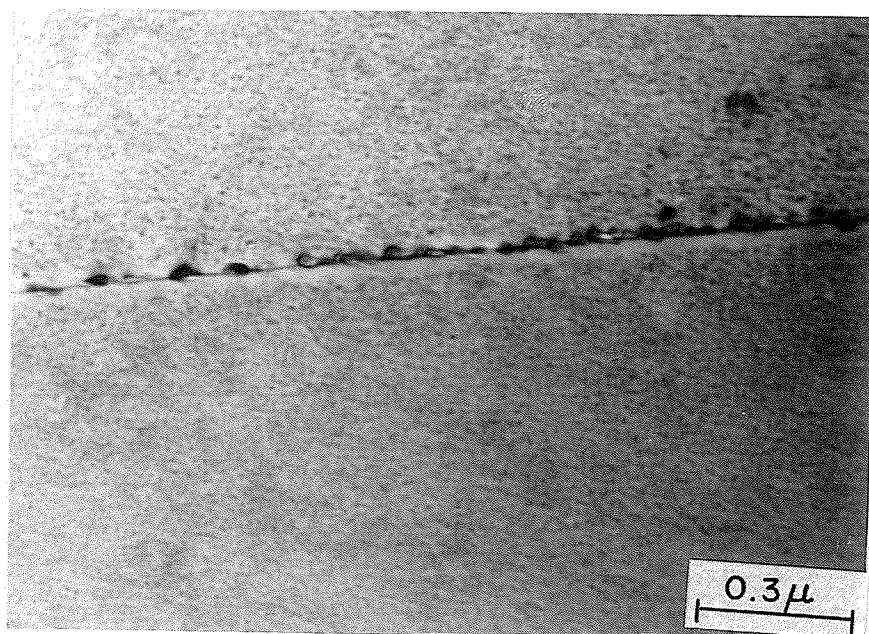


Alloy 5

Figure 29. TEM photomicrographs of alloys 4 and 5 water quenched from SHT, naturally aged for 16 hours and aged at 393K [120°C] for 10 minutes.

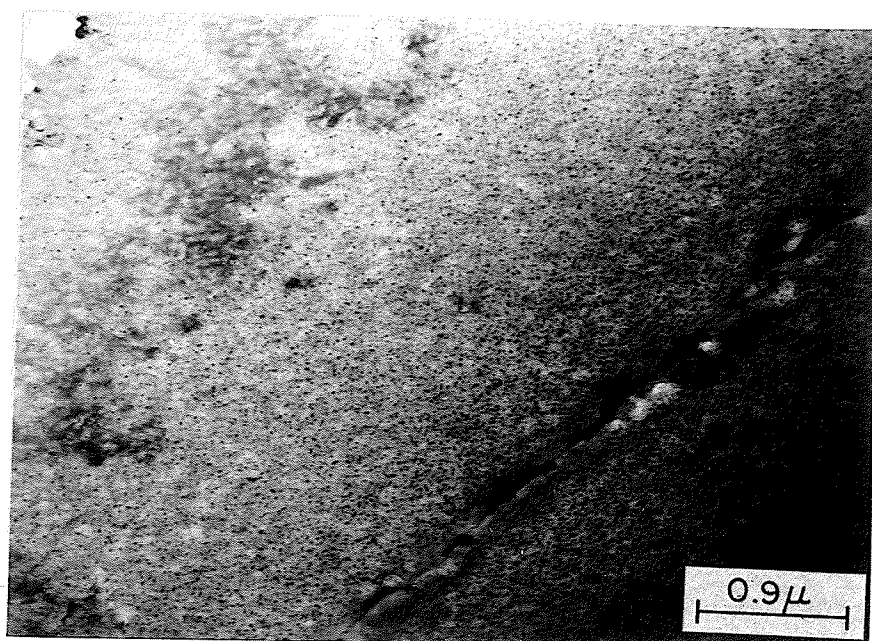


Alloy 4

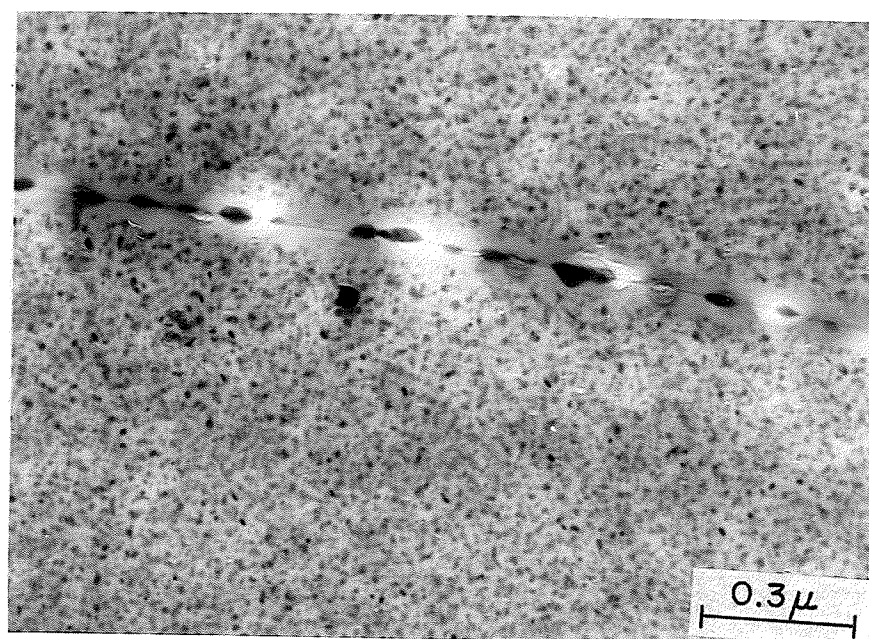


Alloy 5

Figure 30. TEM photomicrographs of alloys 4 and 5 water quenched from SHT, naturally aged for 16 hours and aged at 393K [120°C] for 300 hours.



Alloy 4



Alloy 5

Figure 31. TEM photomicrographs of alloys 4 and 5 water quenched from SHT, naturally aged for 16 hours and aged at 393K [120°C] for 2000 hours.

quenching from solution heat treatment an endothermic reaction took place at approximately 383K [110°C] as shown in Figure 32. No reactions were observed when the same alloy was heated in the differential scanning calorimeter immediately after water quenching from solution heat treatment (Figure 33). This would suggest that in naturally aged specimens a dissolution of precipitates first occurs before the main precipitation starts. Such a dissolution was not observed in specimens which were heated without any prior natural aging.

4.2. Stress Corrosion Behaviour

When the hardness and tensile properties of the two alloys had been determined it was decided to establish the stress corrosion cracking behaviour of the microstructures produced after the heat treatments described in Chapter 3. Susceptibility to stress-corrosion cracking was studied with the slow strain-rate technique and the susceptibility of each microstructure was assessed by determining the influence of variables such as, environment, zirconium content, test strain rate, aging time and temperature, and cooling rate from solution heat treatment temperature on the SCC index, I_{SCC} . I_{SCC} is defined as the ratio of a certain parameter, such as percentage elongation, percentage reduction in area, maximum stress attained during the test, total time to

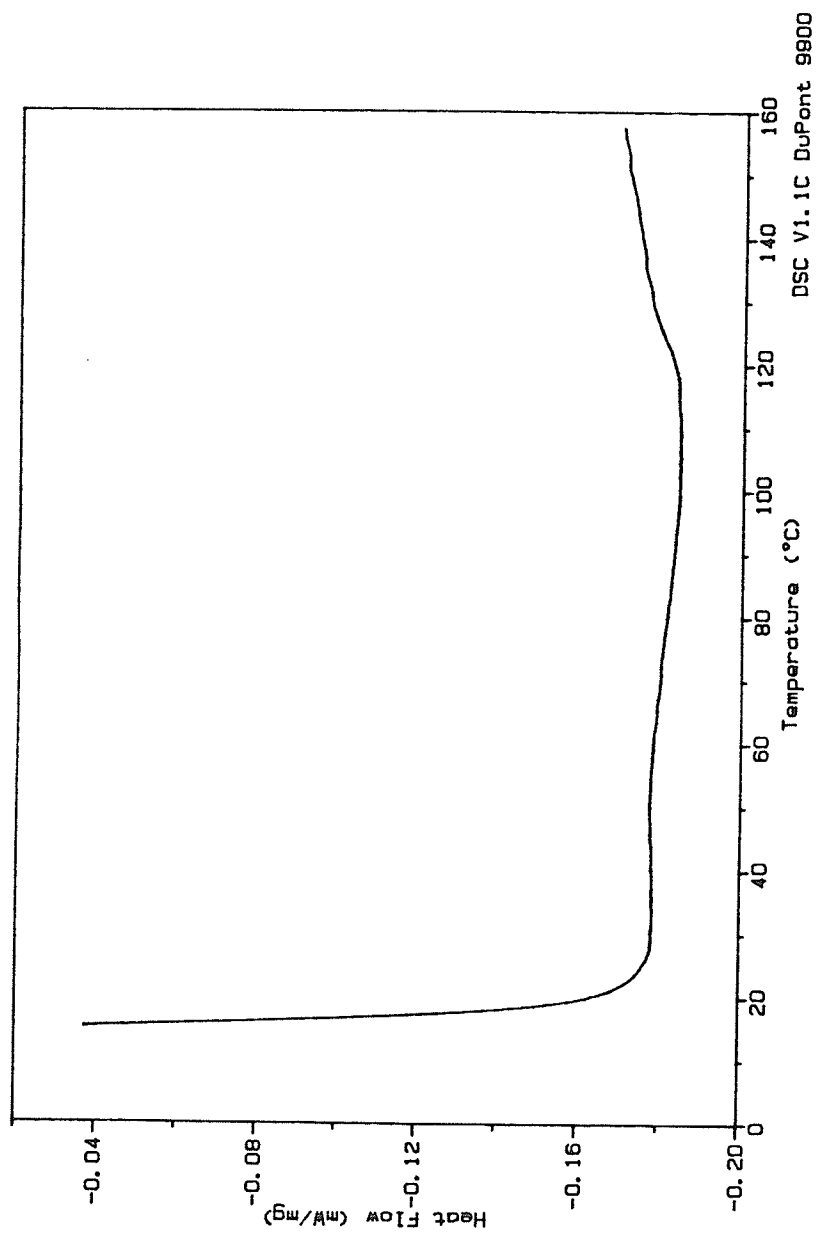


Figure 32. Effect of heating on heat flow in alloy 5 water quenched from SHT and naturally aged for 16 hours.

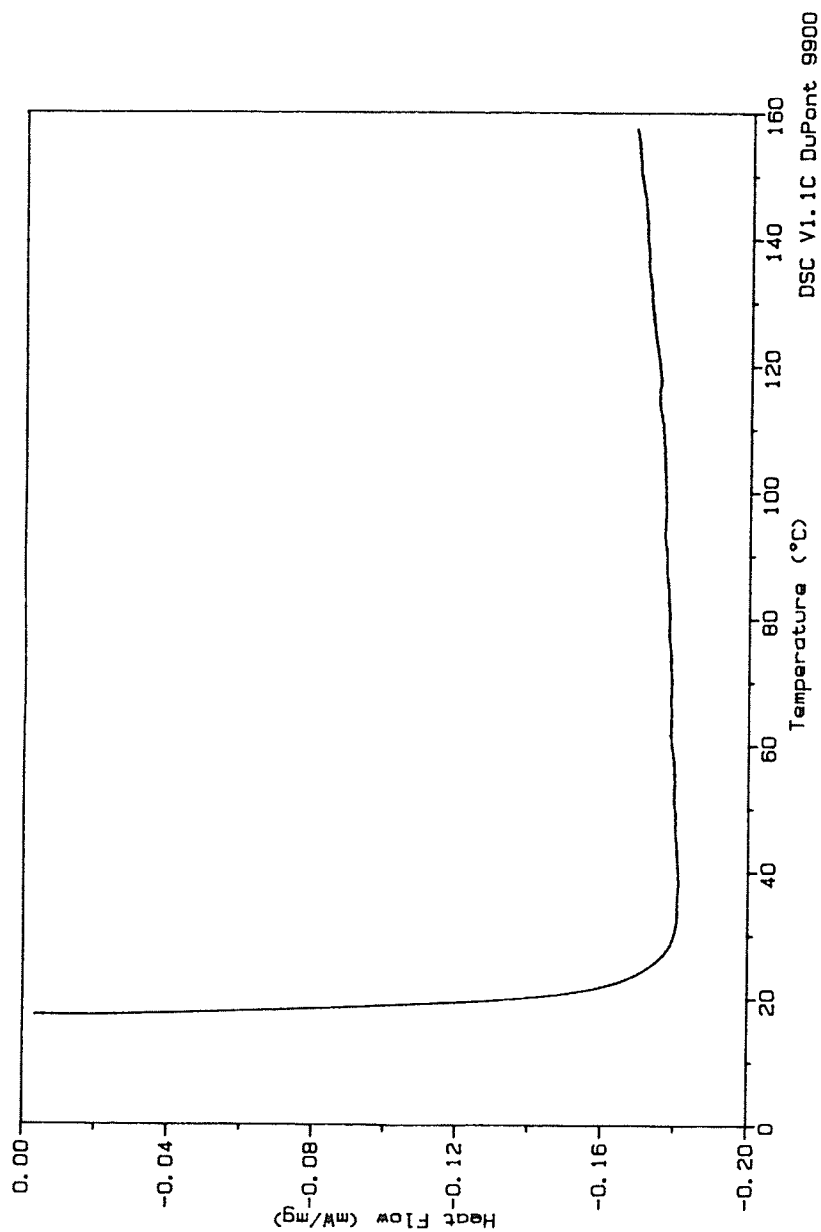


Figure 33. Effect of heating on heat flow in alloy 5 water quenched from SHT without natural aging.

failure etc., as measured from the slow strain-rate test, for a sample tested in aggressive environment to that for a sample tested in an inert environment. In this investigation the I_{SCC} is based on ductility measurements as determined by change in total elongation to fracture.

$$I_{SCC} = \frac{\text{total elongation of sample tested in 3.5\% NaCl}}{\text{total elongation of sample tested in oil}}$$

4.2.1. Stress Corrosion Behaviour of Solution Heat Treated Material

The influence of cooling rate from solution heat treatment on the SCC behaviour of alloys 4 and 5 was determined by establishing the effect of environment on ductility loss, and by determining the I_{SCC} . Also, the effect of strain-rate employed on the ductility loss and the I_{SCC} was determined by using initial strain-rates between 4.1×10^{-7} and $4.1 \times 10^{-4} \text{ s}^{-1}$.

The effect of environment on the ductility loss of samples cooled at various rates from solution heat treatment, which indicates susceptibility to SCC, is illustrated in Tables 11 to 14 and Figures 34 to 45. As shown in Figure 34, when alloy 4 was water quenched from solution heat treatment (SHT) and tested at a strain-rate of $4.1 \times 10^{-7} \text{ s}^{-1}$ at room temperature its total elongation to fracture decreased from 41% when tested in silicone oil to 9% when tested in 3.5%

TABLE 11

Slow Strain-Rate Test Results for Alloys 4 and 5, Naturally Aged for 16 Hours. Tested at $\dot{\epsilon}=4.1 \times 10^{-4} \text{ s}^{-1}$

Alloy	Cooling from SHT	Test Medium	σ_y (MPa)	σ_u (MPa)	Total El., %
4	Water Quenched	Oil	96.0	240.0	42.8
4	Water Quenched	NaCl	91.9	232.8	41.3
5	Water Quenched	Oil	112.3	254.0	42.8
5	Water Quenched	NaCl	108.5	257.4	42.8
4	Air Cooled	Oil	90.4	229.1	38.4
4	Air Cooled	NaCl	91.4	231.7	39.9
5	Air Cooled	Oil	105.1	252.8	45.8
5	Air Cooled	NaCl	108.1	252.5	45.8
4	Block Cooled	Oil	88.5	227.5	41.3
4	Block Cooled	NaCl	90.1	214.8	34.0
5	Block Cooled	Oil	108.3	245.5	44.3
5	Block Cooled	NaCl	109.9	248.0	42.8

TABLE 12

Slow Strain-Rate Test Results for Alloys 4 and 5, Naturally Aged for 16 Hours. Tested at $\dot{\epsilon}=4.1 \times 10^{-5} \text{ s}^{-1}$.

Alloy	Cooling from SHT	Test Medium	σ_y (MPa)	σ_u (MPa)	Total El., %
4	Water Quenched	Oil	109.2	251.2	46.6
4	Water Quenched	NaCl	108.0	251.2	41.0
5	Water Quenched	Oil	126.3	270.7	45.0
5	Water Quenched	NaCl	123.3	271.2	45.7
4	Air Cooled	Oil	105.6	243.3	47.5
4	Air Cooled	NaCl	105.1	246.3	46.5
5	Air Cooled	Oil	124.8	265.7	43.1
5	Air Cooled	NaCl	117.0	262.4	45.9
4	Block Cooled	Oil	104.3	237.0	42.8
4	Block Cooled	NaCl	103.7	243.7	40.6
5	Block Cooled	Oil	116.7	259.3	45.6
5	Block Cooled	NaCl	118.8	261.0	44.7

TABLE 13

Slow Strain-Rate Test Results for Alloys 4 and 5,
Naturally Aged for 16 Hours. Tested at
 $\dot{\epsilon}=4.1 \times 10^{-6} \text{ s}^{-1}$.

Alloy	Cooling from SHT	Test Medium	σ_y (MPa)	σ_u (MPa)	Total El., %
4	Water Quenched	Oil	110.9	267.5	45.1
4	Water Quenched	NaCl	118.4	240.0	27.7
5	Water Quenched	Oil	118.4	288.0	45.1
5	Water Quenched	NaCl	128.0	281.4	33.0
4	Air Cooled	Oil	105.1	262.7	48.5
4	Air Cooled	NaCl	105.2	245.8	39.5
5	Air Cooled	Oil	118.6	290.2	49.4
5	Air Cooled	NaCl	113.8	271.7	47.5
4	Block Cooled	Oil	100.8	246.4	43.1
4	Block Cooled	NaCl	99.3	245.9	44.0
5	Block Cooled	Oil	112.7	273.6	45.7
5	Block Cooled	NaCl	113.4	277.3	46.3

TABLE 14

Slow Strain-Rate Test Results for Alloys 4 and 5, Naturally Aged for 16 Hours. Tested at $\dot{\epsilon}=4.1 \times 10^{-7} \text{ s}^{-1}$.

Alloy	Cooling from SHT	Test Medium	σ_y (MPa)	σ_u (MPa)	Total El., %
4	Water Quenched	Oil	89.7	230.2	40.7
4	Water Quenched	NaCl	102.8	167.5	9.6
5	Water Quenched	Oil	110.5	284.2	37.1
5	Water Quenched	NaCl	136.7	257.5	17.6
4	Air Cooled	Oil	97.3	262.4	47.2
4	Air Cooled	NaCl	105.7	198.0	15.7
5	Air Cooled	Oil	97.9	270.8	46.0
5	Air Cooled	NaCl	115.2	246.5	22.3
4	Block Cooled	Oil	96.7	265.0	37.0
4	Block Cooled	NaCl	104.3	243.0	26.6
5	Block Cooled	Oil	107.2	288.0	50.0
5	Block Cooled	NaCl	112.7	286.6	38.9

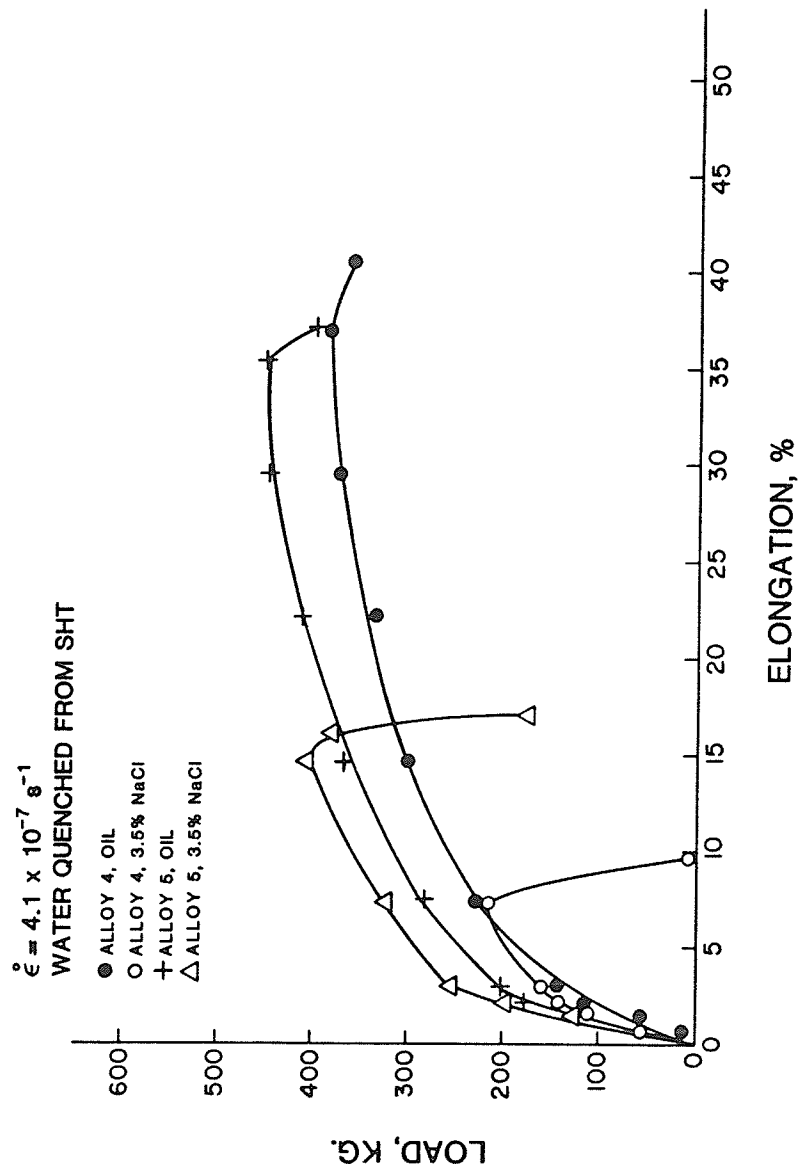


Figure 34. Slow strain-rate test results for alloys 4 and 5 water quenched from SHT and naturally aged for 16 hours. Tested in oil and 3.5% NaCl solution at $\dot{\epsilon} = 4.1 \times 10^{-7} \text{ s}^{-1}$.

NaCl. Under the same experimental conditions the total elongation of alloy 5 decreased from 37% when tested in oil to 16% when tested in 3.5% NaCl. The total elongation of alloy 4 air cooled from SHT decreased from 47% when tested in oil to 16% when tested in 3.5% NaCl, whereas that of alloy 5 air cooled from SHT decreased from 46% when tested in oil to 22% when tested in 3.5% NaCl, Figure 35. When both alloys were block air cooled from SHT the total elongation of alloy 4 decreased from 37% when tested in oil to 26.5% when tested in 3.5% NaCl, and that of alloy 5 decreased from 50 to 38% when tested in oil and 3.5% NaCl respectively, as shown in Figure 36. These results indicate that as the cooling rate from SHT increases, the resistance to SCC as indicated by total percentage elongation decreases, and also that the zirconium containing alloy 5 is more resistant to SCC than alloy 4. Similar behavior was observed at higher initial strain-rates up to $4.1 \times 10^{-4} \text{s}^{-1}$. As seen in Figures 37 through 45 the ductility of both alloys was lower when tested in 3.5% NaCl than when tested in oil. It was also observed that at higher initial strain-rates the ductility loss decreased, which indicates that the SCC behaviour of these alloys is best determined at initial strain-rates lower than $4.1 \times 10^{-5} \text{s}^{-1}$.

The SCC behaviour of the two alloys was also evaluated by determining I_{SCC} for variously cooled alloys tested at various strain rates. As shown in Table 15 and Figure 46, I_{SCC}

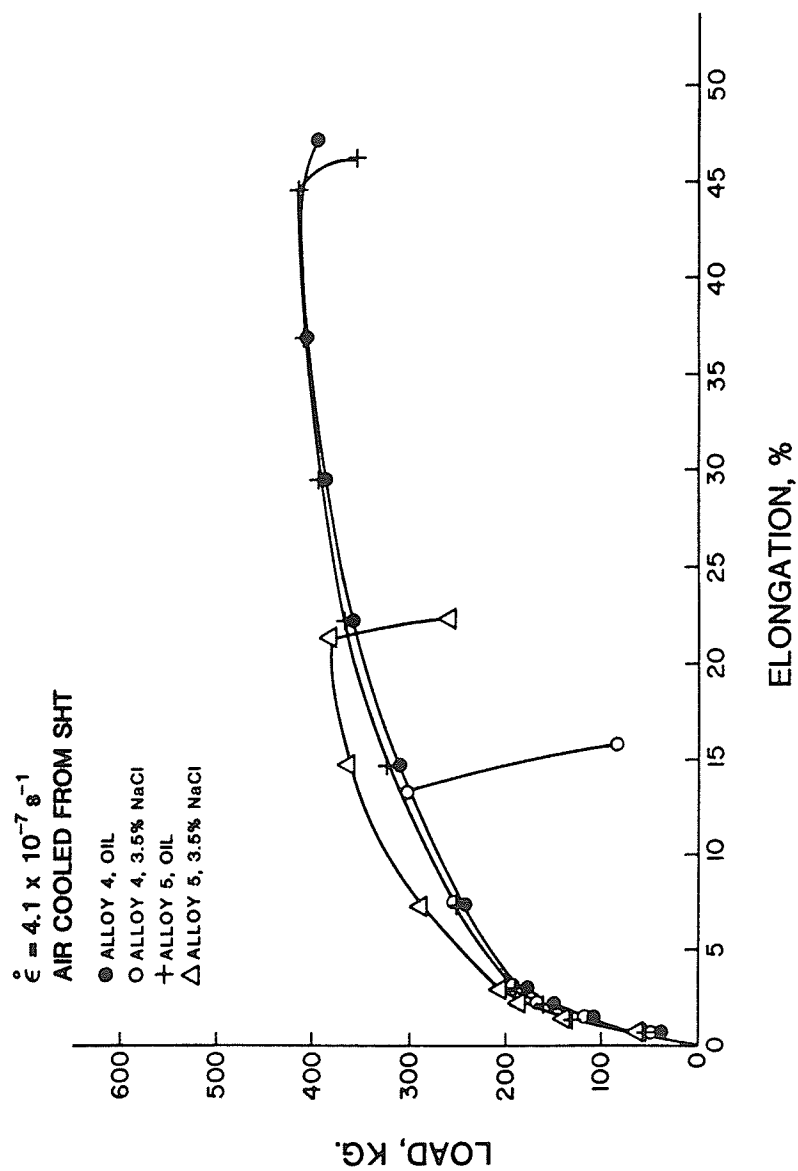


Figure 35. Slow strain-rate test results for alloys 4 and 5 air cooled from SHT and naturally aged for 16 hours. Tested in oil and 3.5% NaCl solution at $\dot{\epsilon}=4.1 \times 10^{-7} \text{ s}^{-1}$.

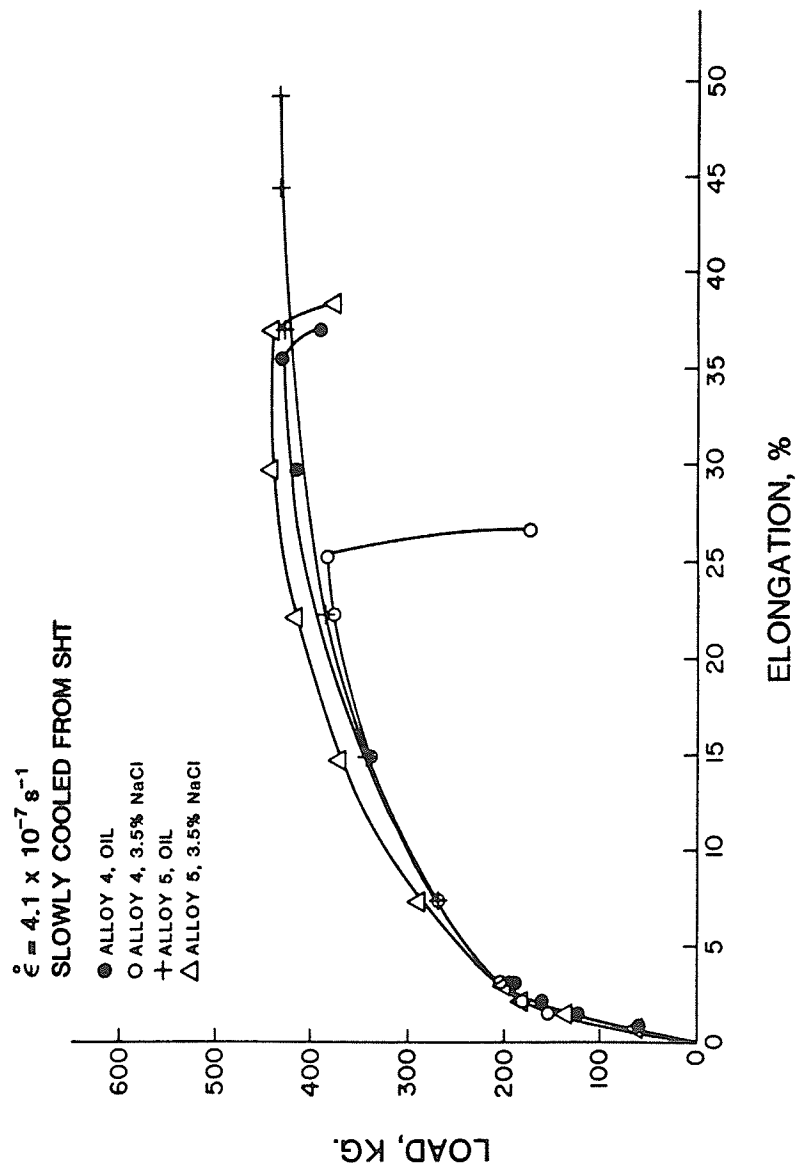


Figure 36. Slow strain-rate test results for alloys 4 and 5 air cooled in a block from SHT and naturally aged for 16 hours. Tested in oil and 3.5% NaCl solution at $\dot{\epsilon} = 4.1 \times 10^{-7} \text{ s}^{-1}$.

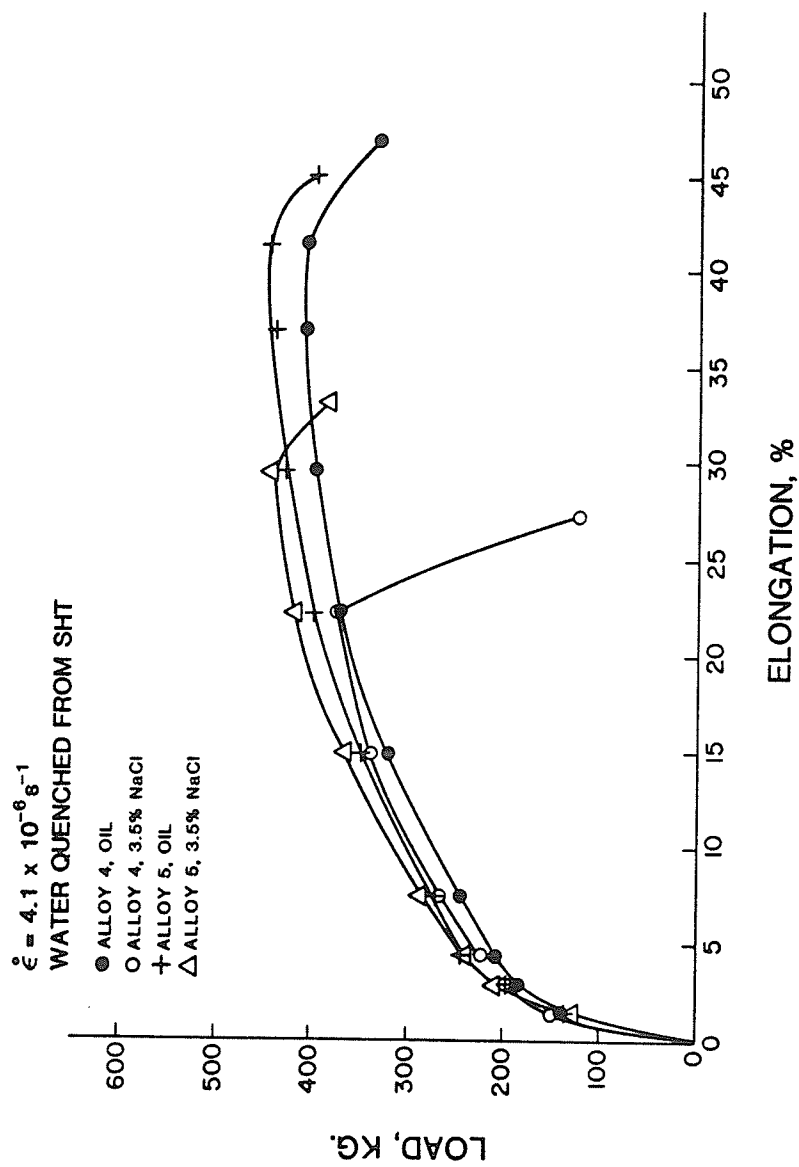


Figure 37. Slow strain-rate test results for alloys 4 and 5 water quenched from SHT and naturally aged for 16 hours. Tested in oil and 3.5% NaCl solution at $\dot{\epsilon} = 4.1 \times 10^{-6} \text{ s}^{-1}$.

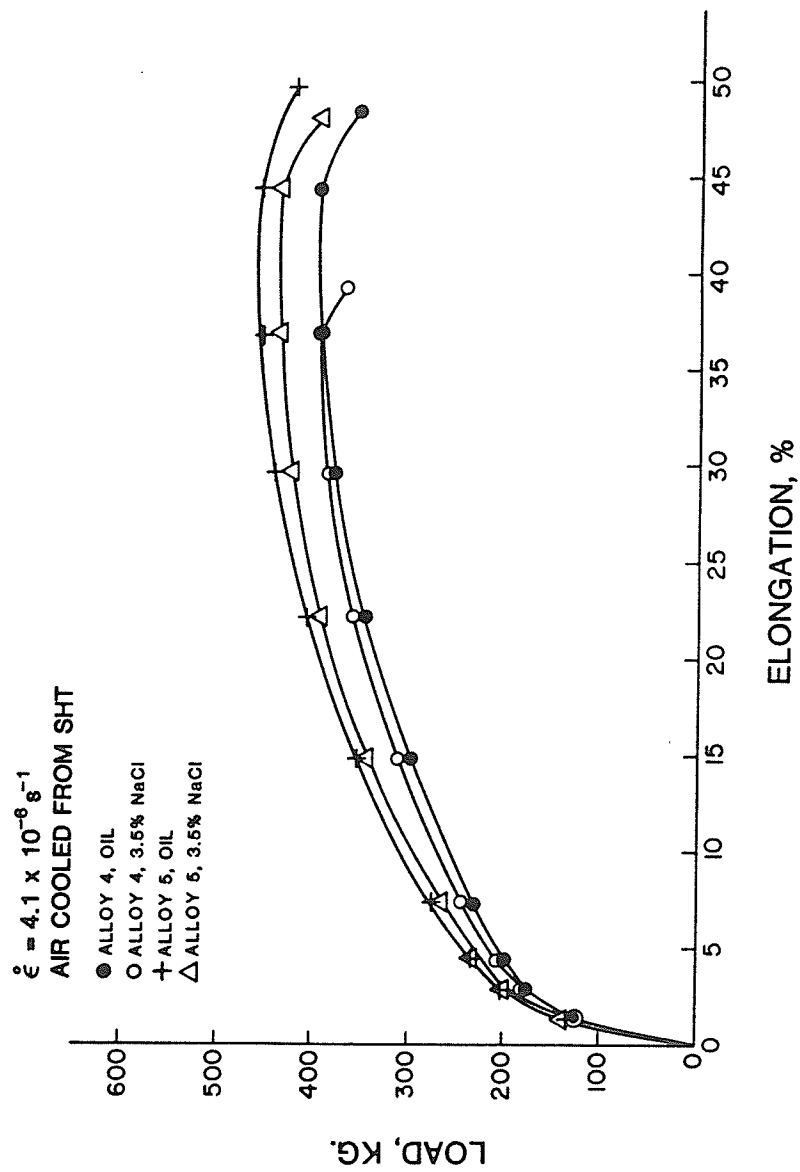


Figure 38. Slow strain-rate test results for alloys 4 and 5 air cooled from SHT and naturally aged for 16 hours. Tested in oil and 3.5% NaCl solution at $\dot{\epsilon} = 4.1 \times 10^{-6} \text{ s}^{-1}$.

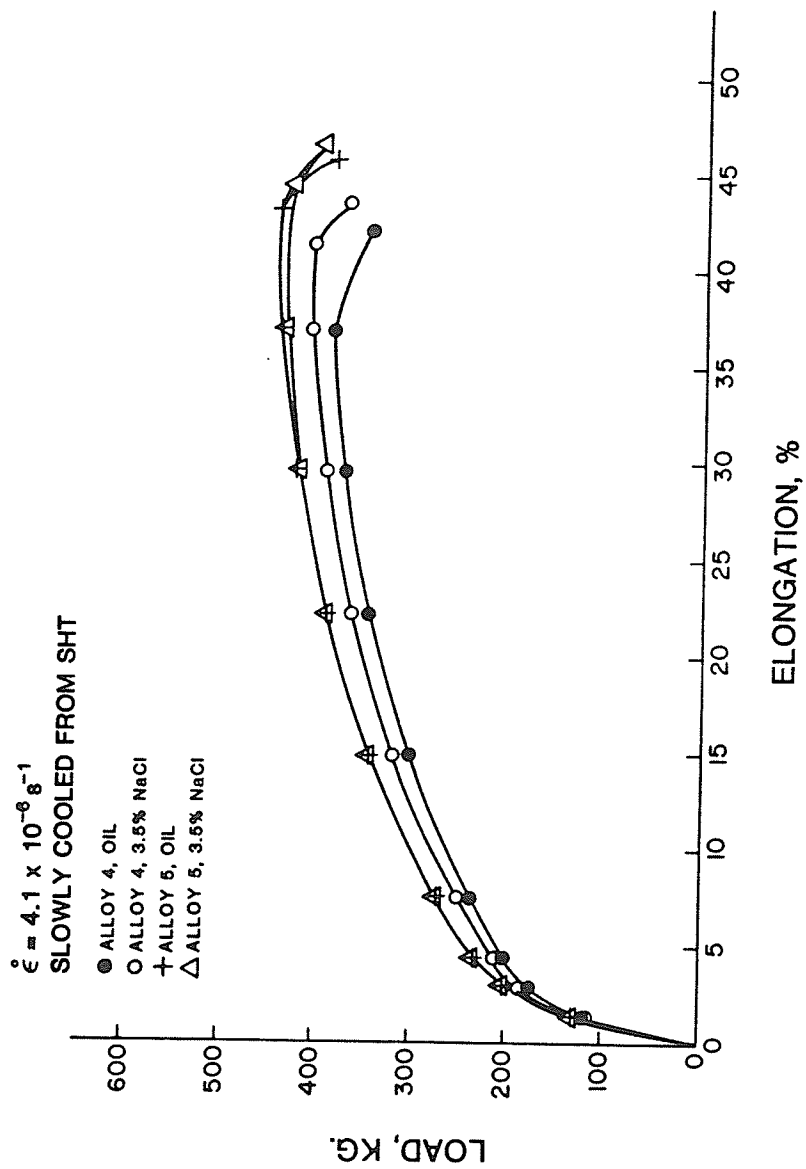


Figure 39. Slow strain-rate test results for alloys 4 and 5 air cooled in a block from SHT and naturally aged for 16 hours. Tested in oil and 3.5% NaCl solution at $\dot{\epsilon} = 4.1 \times 10^{-6} \text{ s}^{-1}$.

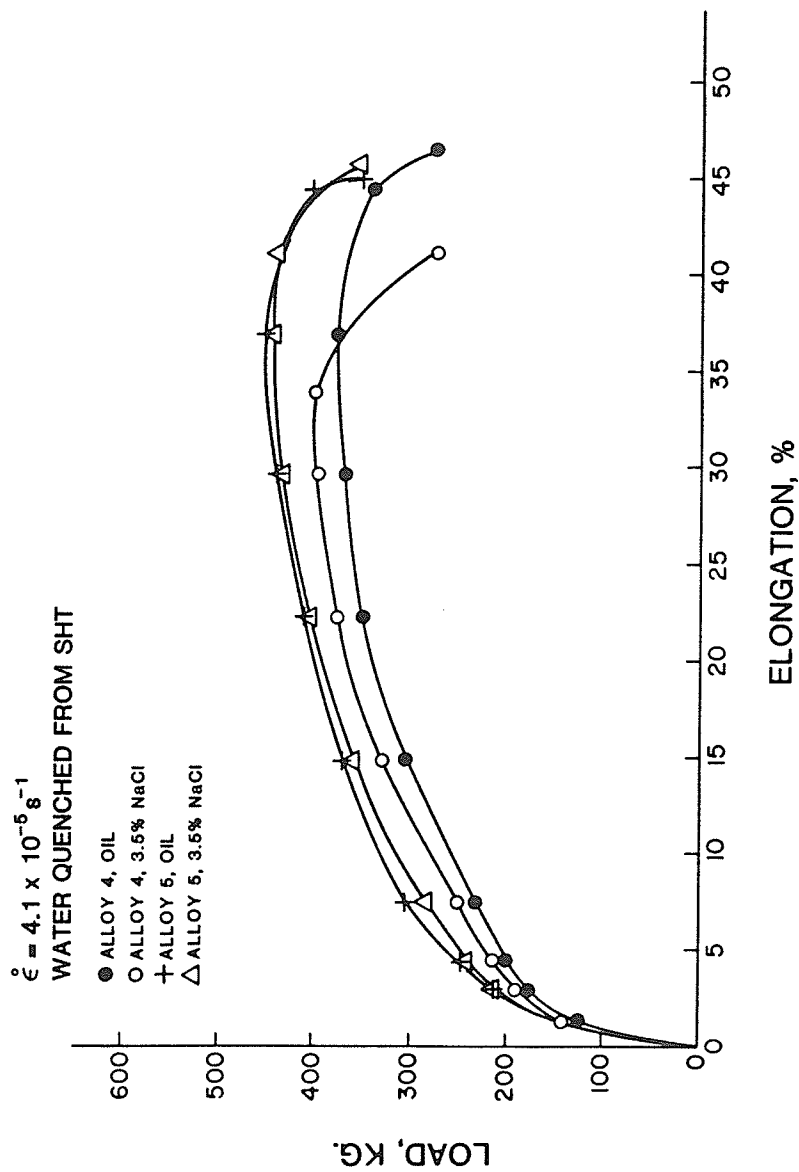


Figure 40. Slow strain-rate test results for alloys 4 and 5 water quenched from SHT and naturally aged for 16 hours. Tested in oil and 3.5% NaCl solution at $\dot{\epsilon} = 4.1 \times 10^{-5} \text{ s}^{-1}$.

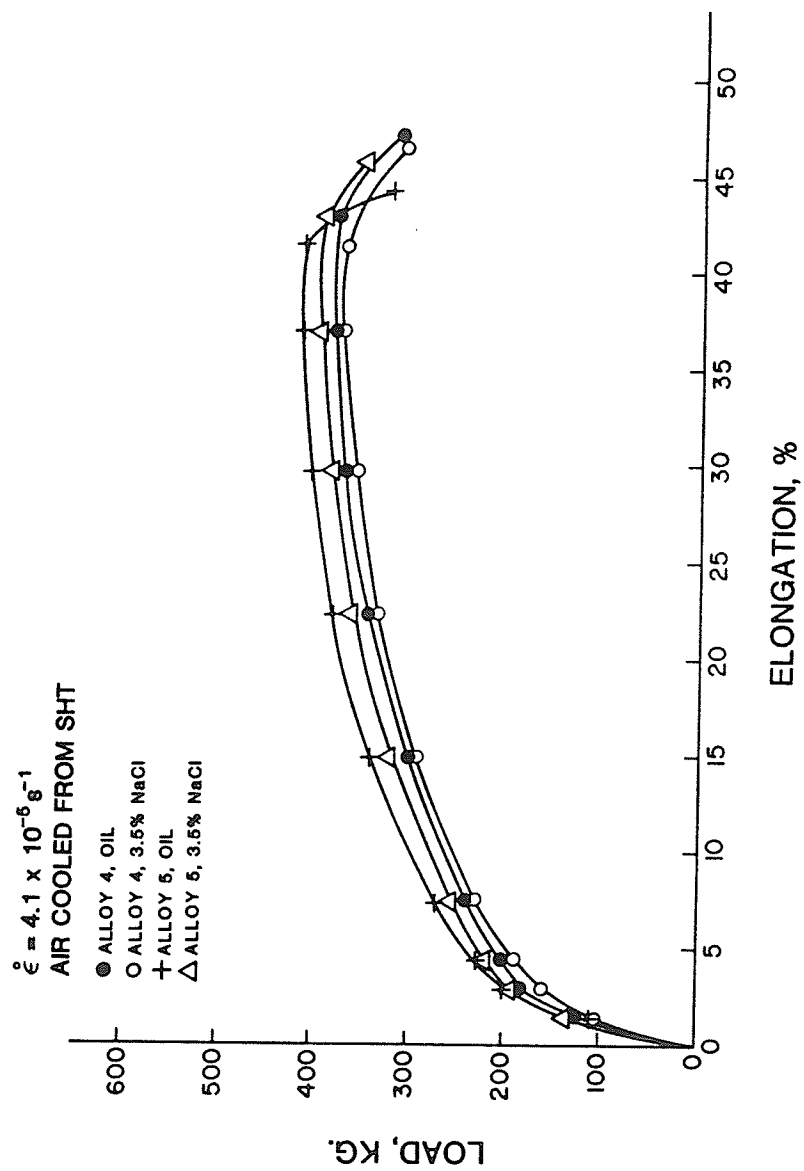


Figure 41. Slow strain-rate test results for alloys 4 and 5 air cooled from SHT and naturally aged for 16 hours. Tested in oil and 3.5% NaCl solution at $\dot{\epsilon} = 4.1 \times 10^{-5} \text{ s}^{-1}$.

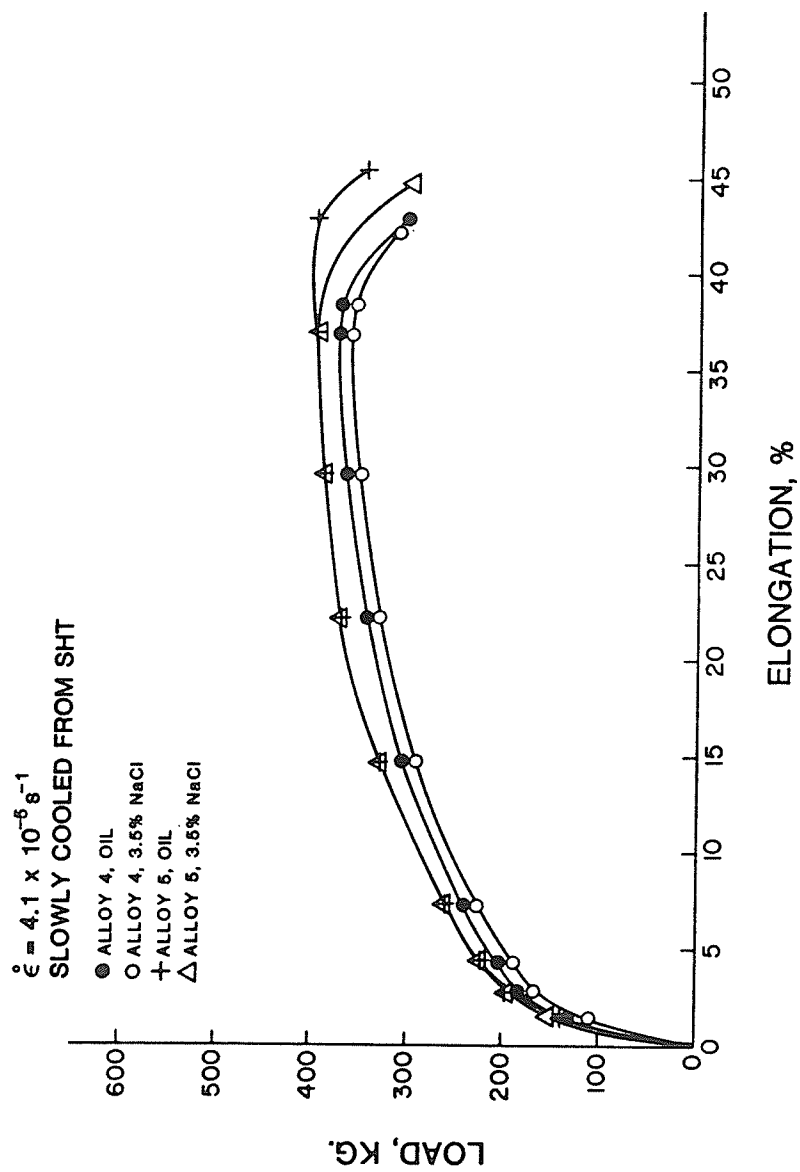


Figure 42. Slow strain-rate test results for alloys 4 and 5 air cooled in a block from SHT and naturally aged for 16 hours. Tested in oil and 3.5% NaCl solution at $\dot{\epsilon} = 4.1 \times 10^{-5} \text{ s}^{-1}$.

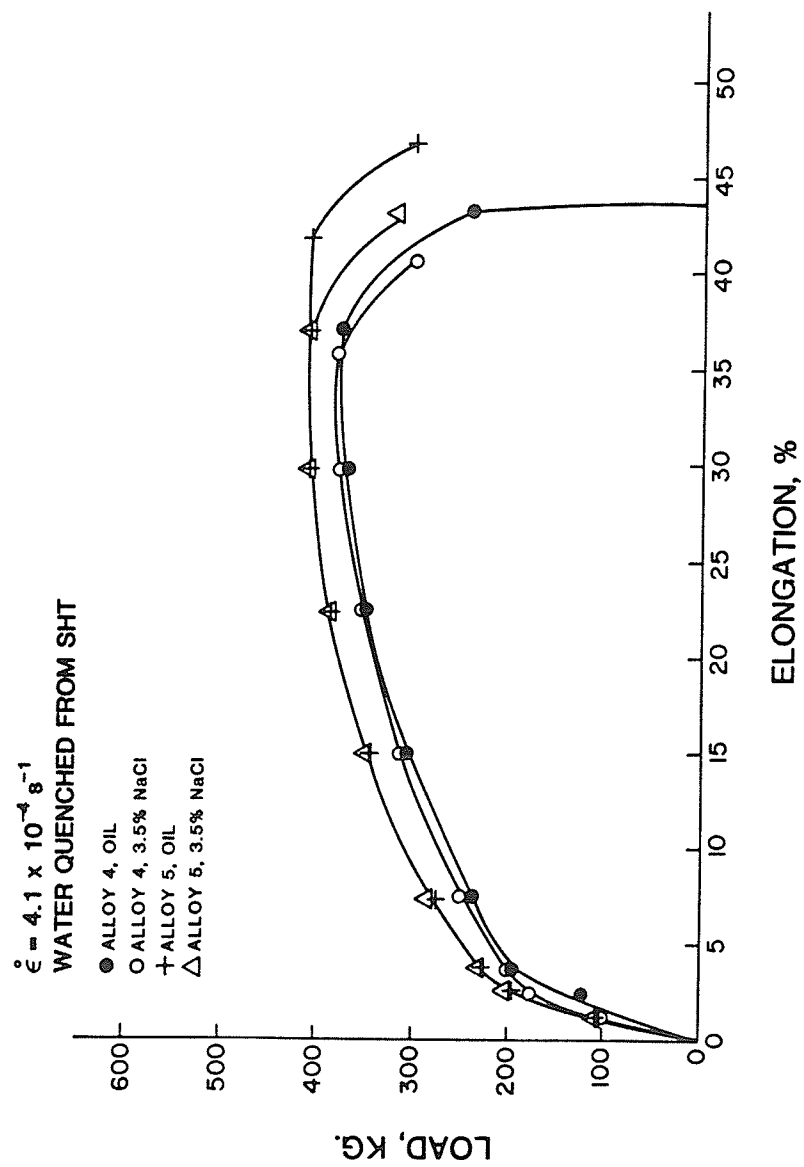


Figure 43. Slow strain-rate test results for alloys 4 and 5 water quenched from SHT and naturally aged for 16 hours. Tested in oil and 3.5% NaCl solution at $\dot{\epsilon} = 4.1 \times 10^{-4} \text{ s}^{-1}$.

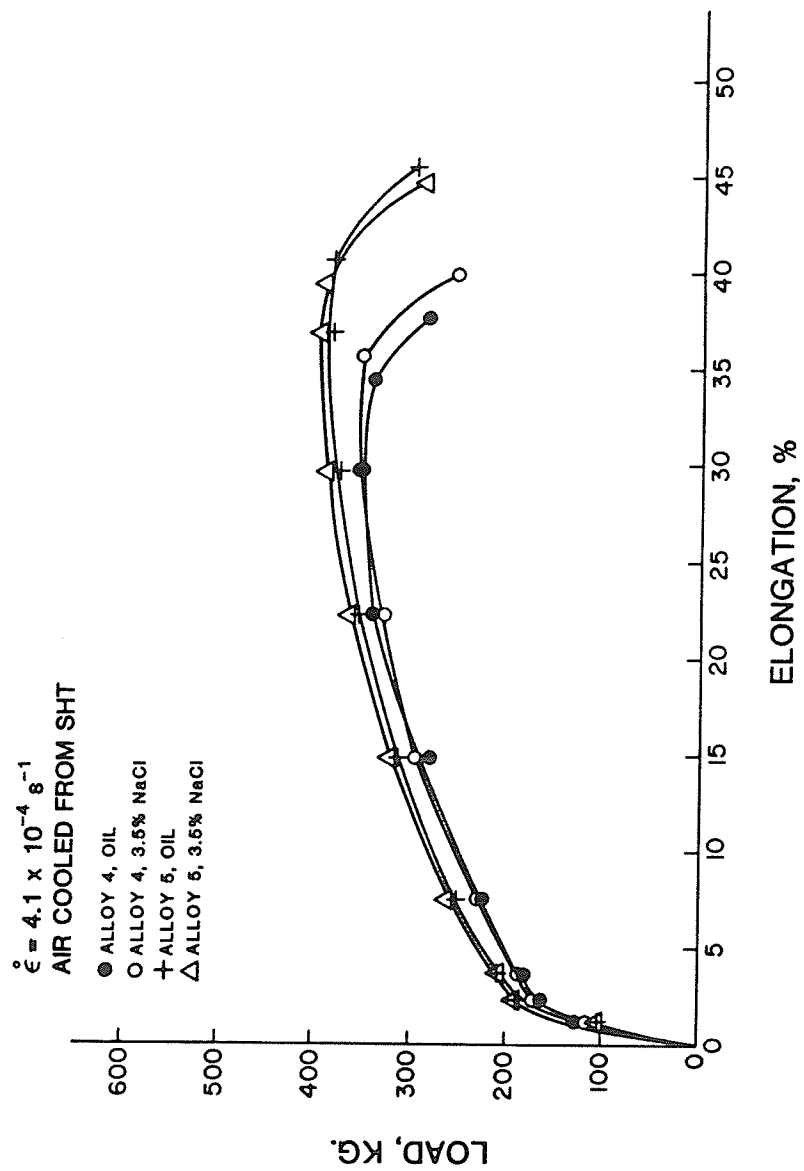


Figure 44. Slow strain-rate test results for alloys 4 and 5 air cooled from SHT and naturally aged for 16 hours. Tested in oil and 3.5% NaCl solution at $\dot{\epsilon} = 4.1 \times 10^{-4} \text{ s}^{-1}$.

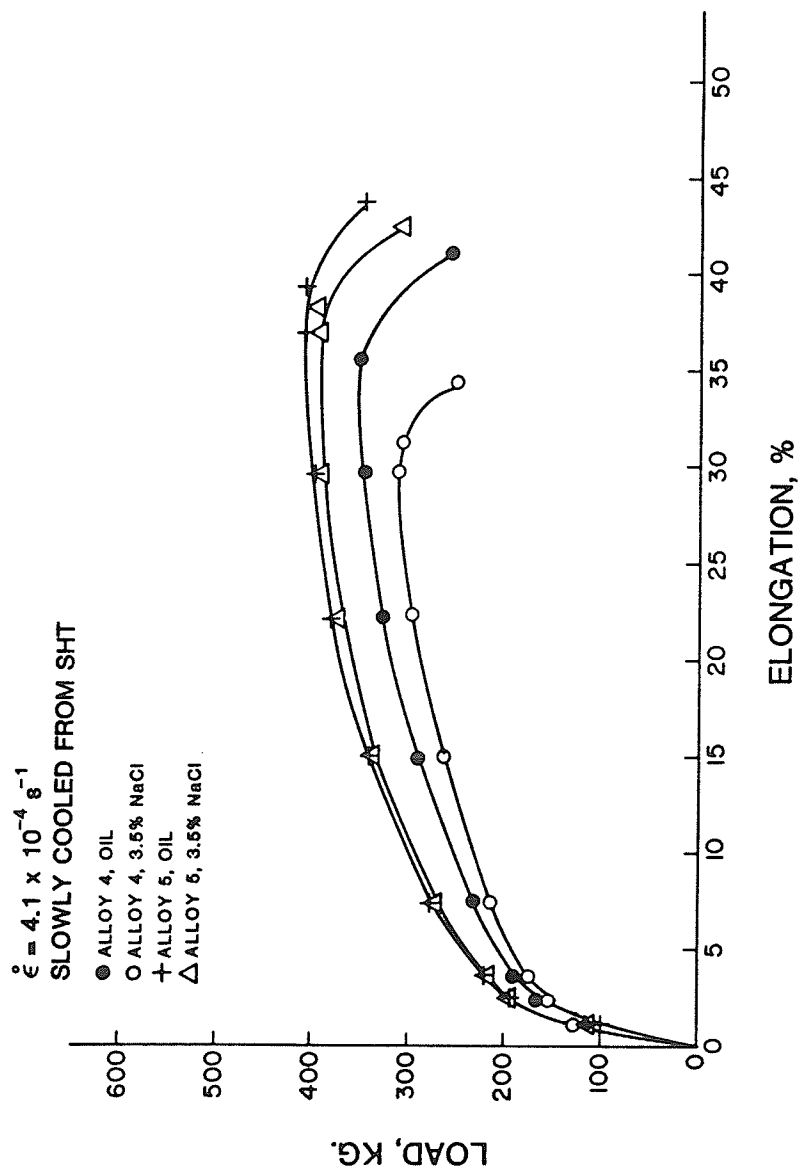


Figure 45. Slow strain-rate test results for alloys 4 and 5 air cooled in a block from SHT and naturally aged for 16 hours. Tested in oil and 3.5% NaCl solution at $\dot{\epsilon} = 4.1 \times 10^{-4} \text{ s}^{-1}$.

for water quenched alloy 5 increased from 0.474 when tested at $4.1 \times 10^{-7} \text{s}^{-1}$ to 1.0 when tested at $4.1 \times 10^{-5} \text{s}^{-1}$ or faster. Iscc for air cooled alloy 5 increased from 0.486 when tested at $4.1 \times 10^{-7} \text{s}^{-1}$ to 0.96 when tested at $4.1 \times 10^{-6} \text{s}^{-1}$ and to 1.0 when tested at $4.1 \times 10^{-5} \text{s}^{-1}$ or faster. Iscc for slowly cooled alloy 5 increased from 0.778 when tested at $4.1 \times 10^{-7} \text{s}^{-1}$ to 1.0 when tested at $4.1 \times 10^{-6} \text{s}^{-1}$ or faster. Iscc for water quenched alloy 4 increased gradually from 0.236 to 0.966 as the strain-rate increased from 4.1×10^{-7} to $4.1 \times 10^{-4} \text{s}^{-1}$, and that of air cooled alloy 4 increased from 0.332 to 1.0 as the strain-rate increased from 4.1×10^{-7} to $4.1 \times 10^{-4} \text{s}^{-1}$. It was also observed that Iscc for slowly cooled alloy 4 increased from 0.72 to 1.0 as the strain-rate increased from 4.1×10^{-7} to $4.1 \times 10^{-6} \text{s}^{-1}$. However, Iscc decreased to 0.821 as the strain-rate was further increased to $4.1 \times 10^{-4} \text{s}^{-1}$, as shown in Table 15 and Figure 47. The effect of zirconium additions on Iscc of 7004 aluminum alloy is shown in Figure 48. The Iscc for alloy 5 is higher than that for alloy 4 for all strain-rates which indicates that the non-recrystallized microstructure of alloy 5 is more resistant to SCC than the fully recrystallized microstructure of alloy 4.

TABLE 15

Stress Corrosion Cracking Index, I_{SCC} *,
for Alloys 4 and 5. Tested at various
Strain Rates

Alloy	Cooling from SHT	I_{SCC}			
		$\dot{\epsilon}=41 \times 10^{-7} \text{ s}^{-1}$	$\dot{\epsilon}=41 \times 10^{-6} \text{ s}^{-1}$	$\dot{\epsilon}=41 \times 10^{-5} \text{ s}^{-1}$	$\dot{\epsilon}=41 \times 10^{-4} \text{ s}^{-1}$
4	Water Quenched	.236	.613	.879	.966
5	Water Quenched	.474	.731	1.016	1.000
4	Air Cooled	.332	.813	.978	1.038
5	Air Cooled	.486	.960	1.065	1.000
4	Block Cooled	.720	1.039	.948	.821
5	Block Cooled	.778	1.029	.981	.967

* I_{SCC} = $\frac{\text{Total Elongation (NaCl)}}{\text{Total Elongation (Oil)}}$

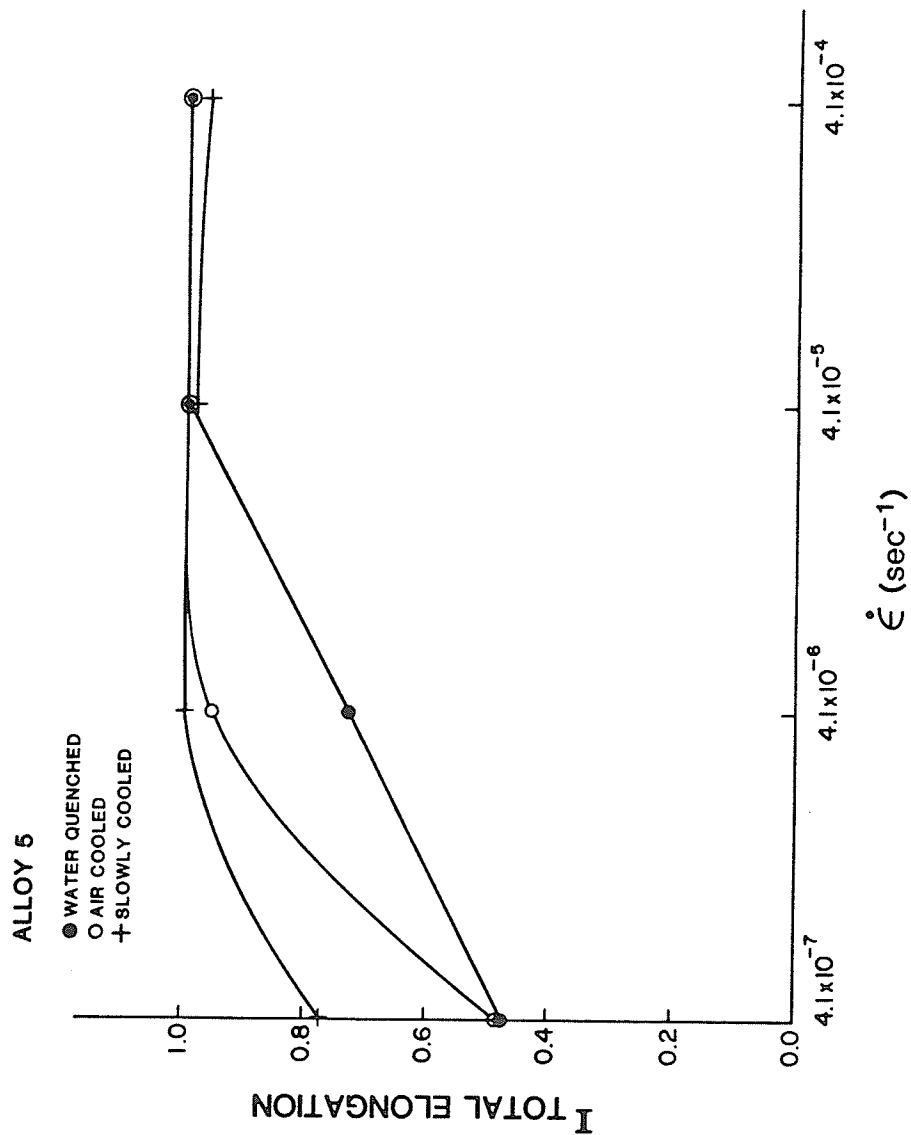


Figure 46. Effect of test strain-rate on Iscc of alloy 5 water quenched, air cooled, and air cooled in a block from SHT and naturally aged for 16 hours.

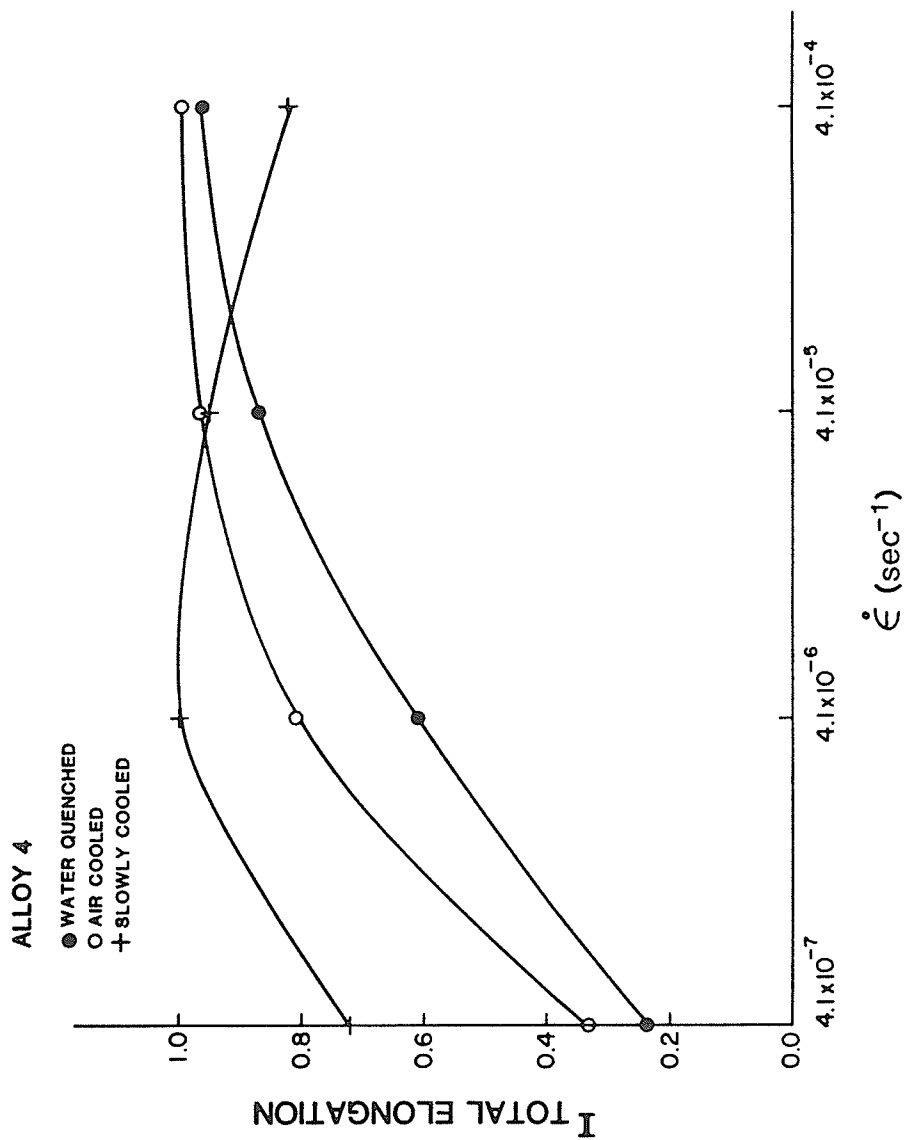


Figure 47. Effect of test strain-rate on Iscc of alloy 4 water quenched, air cooled, and air cooled in a block from SHT and naturally aged for 16 hours.

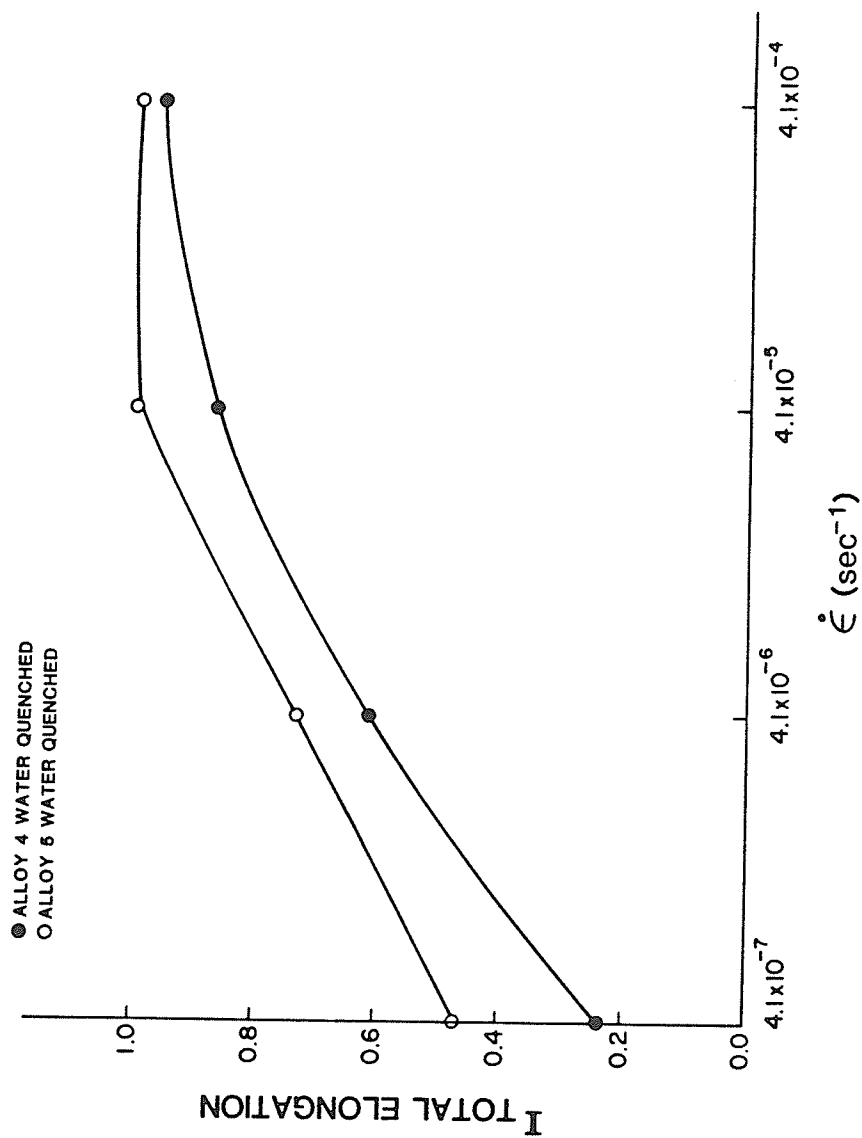


Figure 48. Effect of test strain-rate on Iscc of alloys 4 and 5 water quenched from SHT and naturally aged for 16 hours.

4.2.2. Stress Corrosion Behaviour of Material Aged at 423K [150°C]

The effect of aging at 423K [150°C] on the stress-corrosion behaviour of both alloys was determined by evaluating the stress-corrosion susceptibility index, I_{sc} , for samples which were water quenched, air cooled, or air cooled in a block and aged at 423K [150°C] for up to 1000 hours following natural aging for 16 hours. Once again samples aged for 10 minutes, 24 and 1000 hours, for which the microstructures had been established as reported previously, were tested using the slow strain-rate technique. One specimen in each heat treatment condition described above was tested in silicone oil and one in 3.5% NaCl solution. All tests were performed at room temperature and at a strain-rate of $4.1 \times 10^{-7} \text{ s}^{-1}$, Tables 16-18.

It was observed that the resistance of water quenched alloy 4 increased after 10 minutes of aging at 423K [150°C] as indicated by an increase in the I_{sc} from 0.236 to 0.601. On further aging for 24 hours I_{sc} decreased to 0.527 and once again increased to 0.896 on further aging for 1000 hours, Table 19 and Figure 49. I_{sc} of air cooled alloy 4 increased from 0.332 to 0.902 after 1000 hours of aging at 423K [150°C] which indicates that after this treatment the resistance to SCC of alloy 4 increases with aging time. When alloy 4 was slowly cooled from the solution heat treatment temperature

TABLE 16

Slow Strain-Rate Test Results for Alloys 4 and 5,
 Water Quenched From SHT, Naturally Aged for 16
 Hours, and Artificially Aged at 423K[150°C].
 Tested at $\dot{\epsilon}=4.1 \times 10^{-7} \text{ s}^{-1}$.

Alloy	Age Time	Test Medium	σ_y (MPa)	σ_u (MPa)	Total El., %
4	0	Oil	89.7	230.2	40.7
4	0	NaCl	102.8	167.5	9.6
5	0	Oil	110.5	284.2	37.1
5	0	NaCl	136.7	257.5	17.6
4	10 min.	Oil	116.4	257.3	22.6
4	10 min.	NaCl	53.7	205.4	13.6
5	10 min.	Oil	117.8	272.9	23.1
5	10 min.	NaCl	116.2	244.9	17.8
4	24 hours	Oil	269.4	296.1	20.0
4	24 hours	NaCl	284.4	303.3	10.5
5	24 hours	Oil	252.6	285.9	21.9
5	24 hours	NaCl	247.8	267.0	23.9
4	1000 hours	Oil	196.6	230.9	26.0
4	1000 hours	NaCl	202.2	227.5	23.4
5	1000 hours	Oil	203.6	235.4	24.7
5	1000 hours	NaCl	205.2	232.8	22.2

$$* \quad I_{SCC} = \frac{\text{Total Elongation (NaCl)}}{\text{Total Elongation (Oil)}}$$

TABLE 17

Slow Strain-Rate Test Results for Alloys 4 and 5, Air
Cooled From SHT, Naturally Aged for 16 Hours, and
Artificially Aged at 423K[150°C].
Tested at $\dot{\epsilon}=4.1 \times 10^{-7} \text{ s}^{-1}$.

Alloy	Age Time	Test Medium	σ_y (MPa)	σ_u (MPa)	Total El., %
4	0	Oil	97.3	262.4	47.2
4	0	NaCl	105.7	198.0	15.7
5	0	Oil	97.9	270.8	46.0
5	0	NaCl	115.2	246.5	22.3
4	10 min.	Oil	122.7	245.3	26.0
4	10 min.	NaCl	104.1	204.1	12.6
5	10 min.	Oil	95.1	258.0	29.4
5	10 min.	NaCl	112.7	254.4	26.3
4	24 hours	Oil	264.7	285.7	18.6
4	24 hours	NaCl	257.6	276.4	10.6
5	24 hours	Oil	270.3	292.5	23.1
5	24 hours	NaCl	251.3	270.6	20.9
4	1000 hours	Oil	140.5	183.1	27.2
4	1000 hours	NaCl	142.6	181.5	24.6
5	1000 hours	Oil	143.9	194.4	29.5
5	1000 hours	NaCl	136.1	191.2	29.0

TABLE 18

Slow Strain-Rate Test Results for Alloys 4 and 5, Block
 Cooled from SHT, Naturally Aged for 16 Hours, and
 Artificially Aged at 423K [150°C].
 Tested at $\dot{\epsilon}=4.1 \times 10^{-7} \text{ s}^{-1}$.

Alloy	Age Time	Test Medium	σ_y (MPa)	σ_u (MPa)	Total El., %
4	0	Oil	96.7	265.0	37.0
4	0	NaCl	104.3	243.0	26.6
5	0	Oil	107.2	288.0	50.0
5	0	NaCl	112.7	286.6	38.9
4	10 min.	Oil	68.9	232.6	26.2
4	10 min.	NaCl	72.6	128.1	24.8
5	10 min.	Oil	87.7	296.7	54.3
5	10 min.	NaCl	81.1	262.1	38.0
4	24 hours	Oil	289.7	308.2	22.1
4	24 hours	NaCl	262.2	277.8	10.8
5	24 hours	Oil	248.2	285.4	23.2
5	24 hours	NaCl	224.4	256.0	23.1
4	1000 hours	Oil	--	--	--
4	1000 hours	NaCl	--	--	--
5	1000 hours	Oil	149.7	193.0	28.7
5	1000 hours	NaCl	145.8	186.1	28.4

TABLE 19

Stress Corrosion Cracking Index, I_{sc} *, for Alloys 4 and 5,
 Water Quenched, Air Cooled, or Air Cooled in a Block from
 SHT, Naturally Aged for 16 Hours and Artificially
 Aged at 423K [150°C].
 Tested at $\dot{\epsilon}=4.1 \times 10^{-7} \text{ s}^{-1}$.

Age Time, hrs.	Alloy	I_{sc}		
		Water Quenched	Air Cooled	Block Cooled
0	4	.236	.332	.720
0	5	.474	.486	.778
0.17	4	.601	.483	.946
0.17	5	.769	.897	.700
24	4	.527	.571	.490
24	5	1.056	.904	.994
1000	4	.896	.902	--
1000	5	.898	.985	.985

$$* I_{sc} = \frac{\text{Total Elongation (NaCl)}}{\text{Total Elongation (Oil)}}$$

its resistance to SCC first increased as indicated by an increase in I_{sc} from 0.720 to 0.946 after 10 minutes of aging. However, on further aging for up to 24 hours I_{sc} decreased to 0.490, Table 19 and Figure 49.

The effect of aging time on the SCC resistance of alloy 5 aged at 423K [150°C] is shown in Table 19 and Figure 50. It was observed that the value of I_{sc} of the water quenched alloy 5 increased from 0.474 to 1.000 after 24 hours of aging. However, it decreased to 0.898 after 1000 hours. After 10 minutes of aging I_{sc} of air cooled alloy 5 increased from 0.486 to 0.897 and then gradually increased to 0.985 on further aging for up to 1000 hours. A different trend was observed in the I_{sc} behaviour of slowly cooled alloy 5. An initial drop in I_{sc} from 0.778 to 0.700 was observed after 10 minutes of aging. However, I_{sc} increased to 0.994 after 24 hours and remained approximately constant on further aging for up to 1000 hours at 423K [150°C], Figure 50.

4.2.3. Stress Corrosion Behaviour of Material Aged at 393K [120°C]

The effect of aging at 393K [120°C] on the stress corrosion behaviour was determined by solution heat treating samples of both alloys at 773K [500°C] for 30 minutes, followed by water quenching to room temperature, holding at room temperature for 16 hours, and aging at 393K [120°C] for up

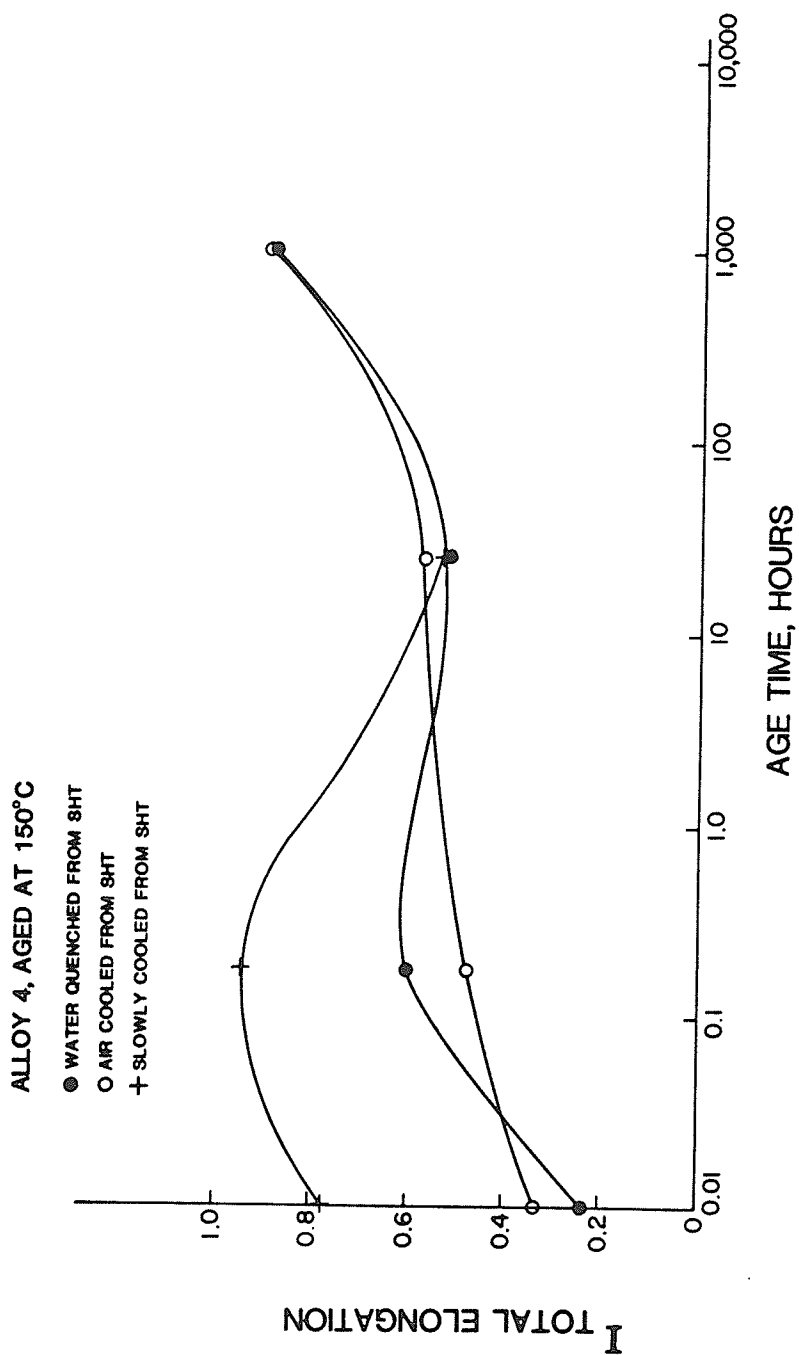


Figure 49. Effect of aging time on Iscc of alloy 4 water quenched, air cooled, and air cooled in a block from SHT, naturally aged for 16 hours and aged at 423K [150°C]. Tested at $\dot{\epsilon}=4.1 \times 10^{-7} \text{ s}^{-1}$.

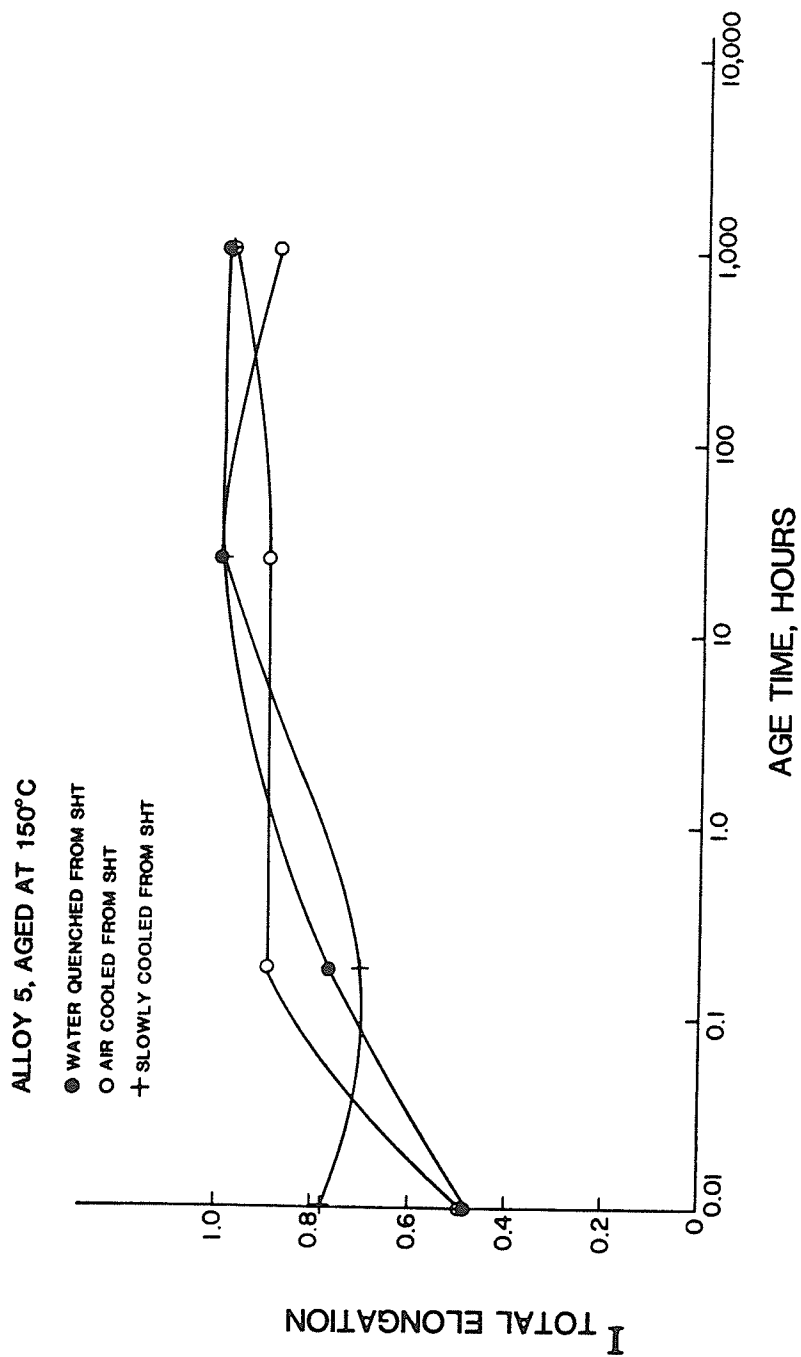


Figure 50. Effect of aging time on I SCC of alloy 5 water quenched, air cooled, and air cooled in a block from SHT, naturally aged for 16 hours and aged at 423K [150°C]. Tested at $\dot{\epsilon}=4.1 \times 10^{-7} \text{ s}^{-1}$.

to 2000 hours. The SCC behaviour was assessed by testing samples aged for 10 minutes, 300 and 2000 hours using the slow strain-rate testing technique. One specimen in each heat treated condition described above was tested in silicone oil and one in 3.5%, by weight NaCl solution. All tests were performed at a strain-rate of $4.1 \times 10^{-7} \text{s}^{-1}$ and at room temperature (Table 20). The stress corrosion behaviour was evaluated by determining I_{sc} as a function of aging time, as shown in Table 21 and Figure 51. It was observed that I_{sc} of alloy 4 increased from 0.236 to 0.374 after 10 minutes of aging. However, it remained fairly constant for up to 2000 hours of aging. I_{sc} of alloy 5 remained nearly the same, i.e. 0.474 and 0.427 after aging for 10 minutes and 2000 hours at 393K [120°C]. These results indicate that both alloys remain fairly susceptible to SCC even after long periods of aging at 393K [120°C].

4.3. Fracture Surface Observations

A selected number of specimens tested at an initial strain-rate of $4.1 \times 10^{-7} \text{s}^{-1}$ were examined in both the optical and scanning electron microscopes to evaluate the fracture characteristics of variously treated specimens. It was observed that intergranular cracks perpendicular to the direction of load application were present on the surface of specimens tested in 3.5% NaCl. However, cracks were not seen

TABLE 20

Slow Strain-Rate Test Results for Alloys 4 and 5, Water
Quenched From SHT, Naturally Aged for 16 Hours, and
Artificially Aged at 393K[120°C].
Tested at $\dot{\epsilon}=4.1 \times 10^{-7} \text{ s}^{-1}$.

Alloy	Age Time	Test Medium	σ_y (MPa)	σ_u (MPa)	Total El., %
4	0	Oil	89.7	230.2	40.7
4	0	NaCl	102.8	167.5	9.6
5	0	Oil	110.5	284.2	37.1
5	0	NaCl	136.7	257.5	17.6
4	10 min.	Oil	96.1	297.7	38.8
4	10 min.	NaCl	96.0	217.6	14.5
5	10 min.	Oil	120.1	278.0	37.0
5	10 min.	NaCl	124.0	254.5	17.3
4	300 hours	Oil	349.2	367.6	21.3
4	300 hours	NaCl	345.4	357.9	6.7
5	300 hours	Oil	347.6	372.8	22.8
5	300 hours	NaCl	343.4	362.5	9.9
4	2000 hours	Oil	314.0	345.4	24.1
4	2000 hours	NaCl	259.2	278.1	8.4
5	2000 hours	Oil	292.5	324.3	23.3
5	2000 hours	NaCl	284.0	293.3	9.9

TABLE 21

Stress Corrosion Cracking Index, I_{sc} *
for Alloys 4 and 5, Water Quenched from
SHT, Naturally Aged for 16 Hours and
Artificially Aged at 393K[120°C].
Tested at $\dot{\epsilon}=4.1 \times 10^{-7} \text{ s}^{-1}$.

Age Time, hrs	Alloy	I_{sc}
0	4	.236
	5	.474
0.17	4	.374
	5	.468
300	4	.313
	5	.435
2000	4	.350
	5	.427

*
$$I_{sc} = \frac{\text{Total Elongation (NaCl)}}{\text{Total Elongation (Oil)}}$$

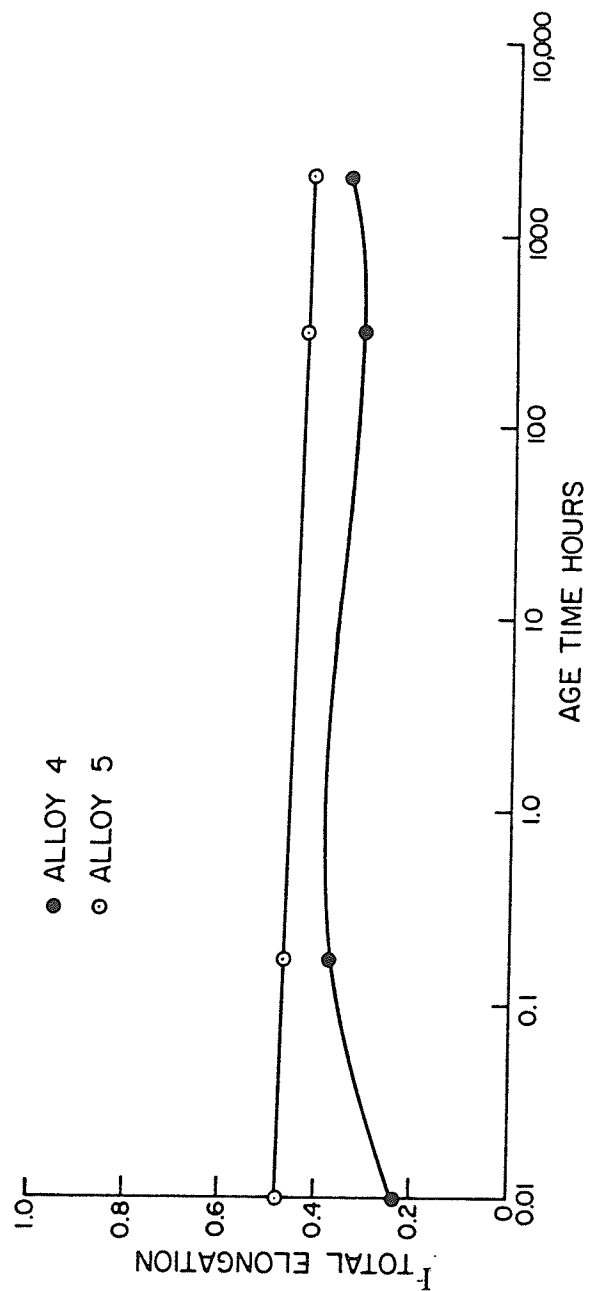


Figure 51. Effect of aging time on I_{scc} of alloys 4 and 5 water quenched from SHT, naturally aged for 16 hours and aged at 393K [120°C]. Tested at $\dot{\epsilon}=4.1 \times 10^{-7} \text{ s}^{-1}$.

in specimens tested in silicone oil, (Figures 52 to 57). The fracture surfaces of specimens solution heat treated at 773K [500°C], water quenched, air cooled or air cooled in block, naturally aged for 16 hours, and tested at $4.1 \times 10^{-7} \text{s}^{-1}$ in either 3.5% NaCl or silicone oil were also examined in the SEM. It was observed that the specimens tested in oil had a predominantly ductile dimpled fracture appearance. However, those tested in 3.5% NaCl exhibited a typical brittle fracture appearance with facets containing striations. It was also observed that the amount of brittle fracture decreased as the cooling rate from solution heat treatment decreased, Figures 58-63.

A selected number of specimens which were artificially aged at 423K [150°C] or 393K [120°C] after water quenching from solution heat treatment and tested at $4.1 \times 10^{-7} \text{s}^{-1}$ in 3.5% NaCl as well as in oil were examined at low magnifications. As seen in Figures 64-66, both alloys exhibited cracks perpendicular to the direction of load application when tested in 3.5% NaCl after aging at 423K [150°C] for up to 1000 hours, whereas cracks were not present on the surface of samples tested in oil. It was also observed that alloy 4 exhibited a higher number of cracks than alloy 5. A similar behaviour was observed when both alloys were aged at 393K [120°C], as shown in Figures 67-69. Cracks were only present on the surface of samples tested in the 3.5% solution of NaCl. It was also observed that samples from both

alloys exhibited a similar number of cracks unlike samples aged at 423K [150°C].

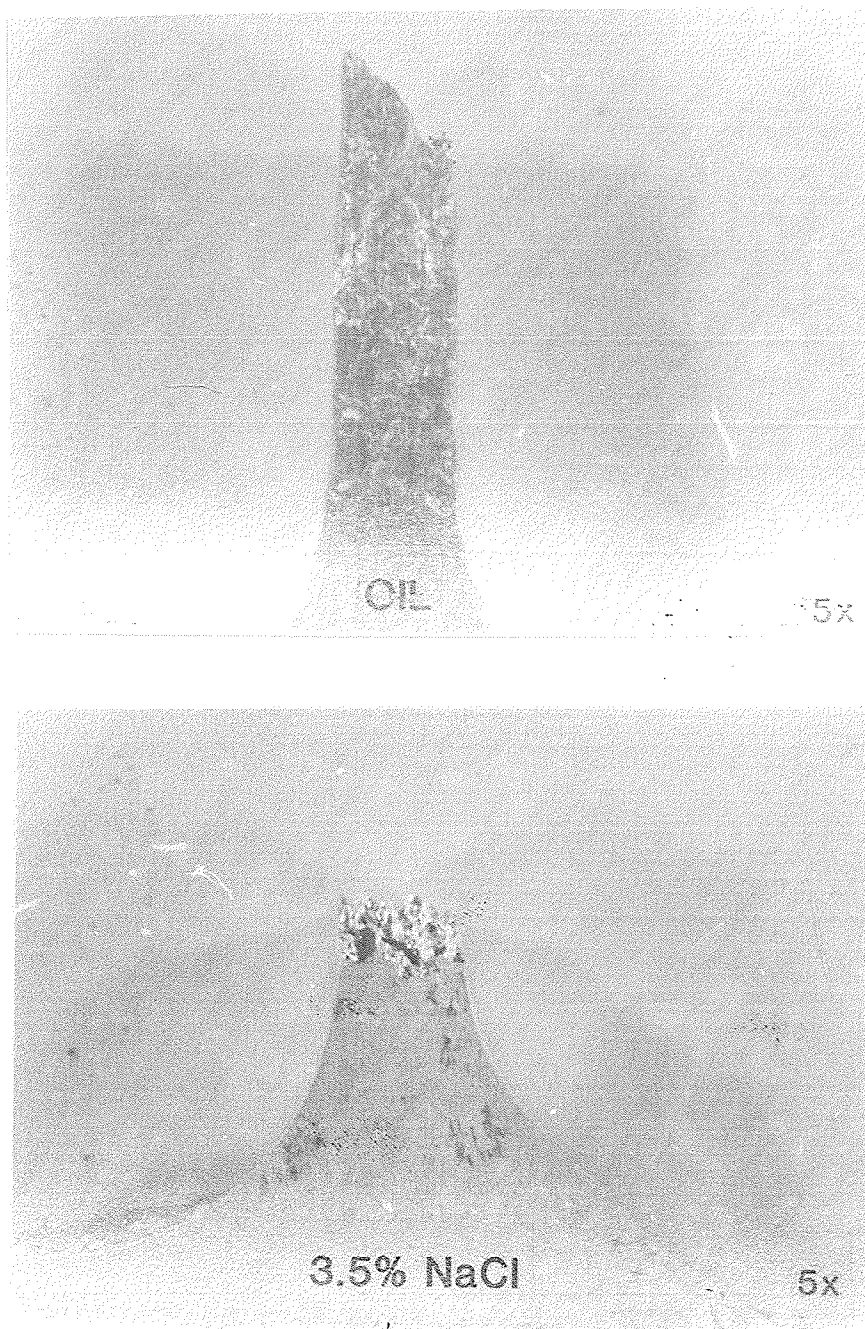


Figure 52. Slow strain-rate test specimens of alloy 4 water quenched from SHT and naturally aged for 16 hours. Tested in oil and 3.5% NaCl solution at $\dot{\epsilon}=4.1 \times 10^{-7} \text{s}^{-1}$.

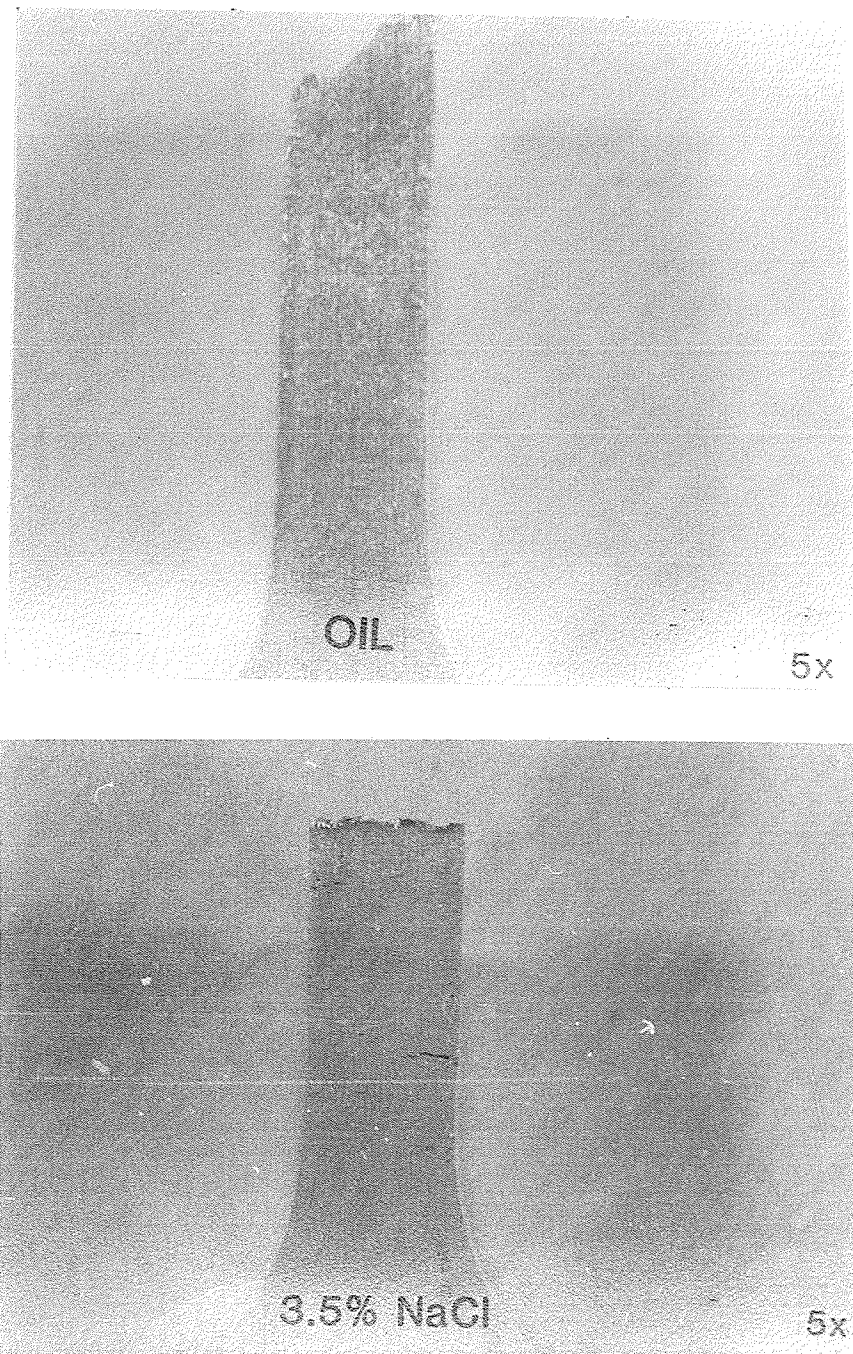


Figure 53. Slow strain-rate test specimens of alloy 5 water quenched from SHT and naturally aged for 16 hours. Tested in oil and 3.5% NaCl solution at $\dot{\epsilon}=4.1 \times 10^{-7} \text{ s}^{-1}$.

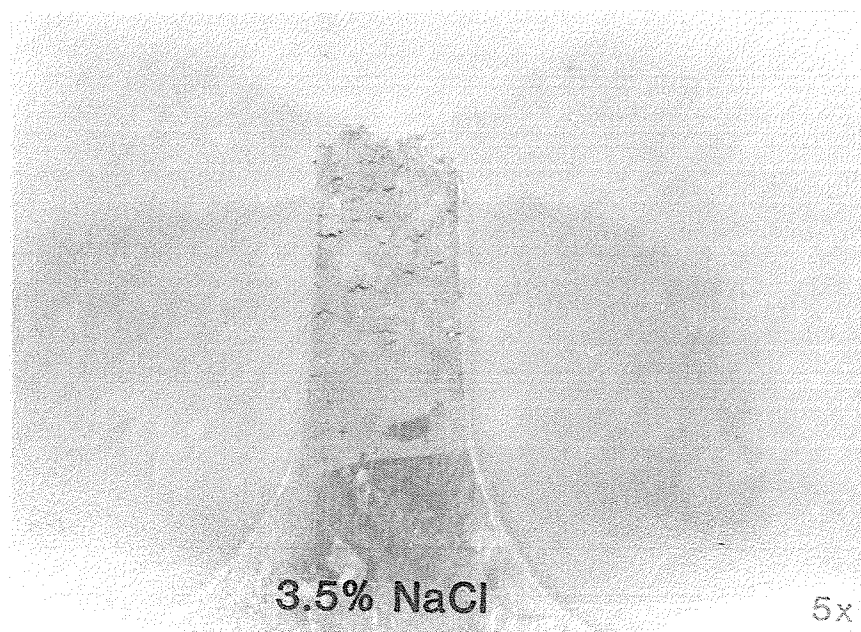
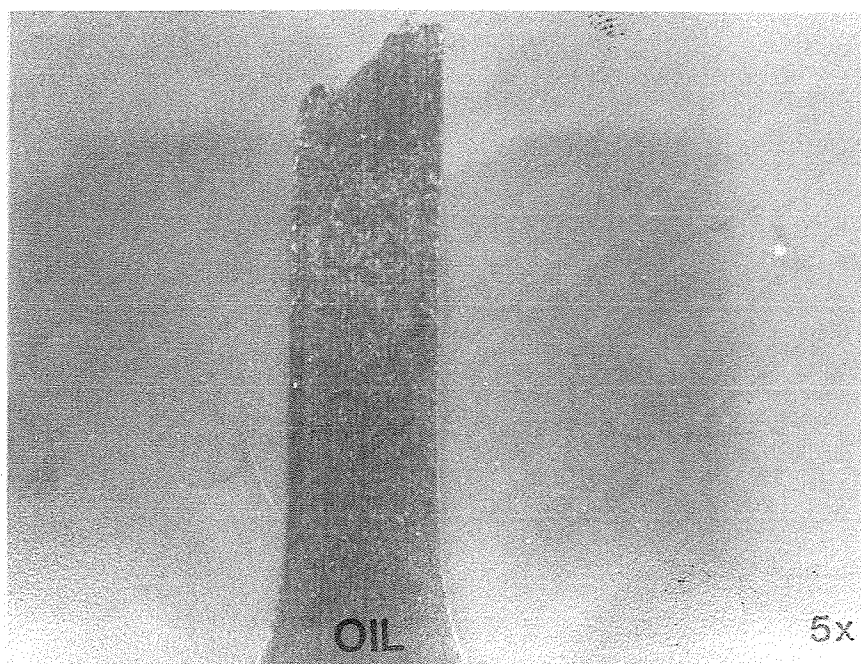


Figure 54. Slow strain-rate test specimens of alloy 4 air cooled from SHT and naturally aged for 16 hours. Tested in oil and 3.5% NaCl solution at $\dot{\epsilon}=4.1 \times 10^{-7} \text{ s}^{-1}$.

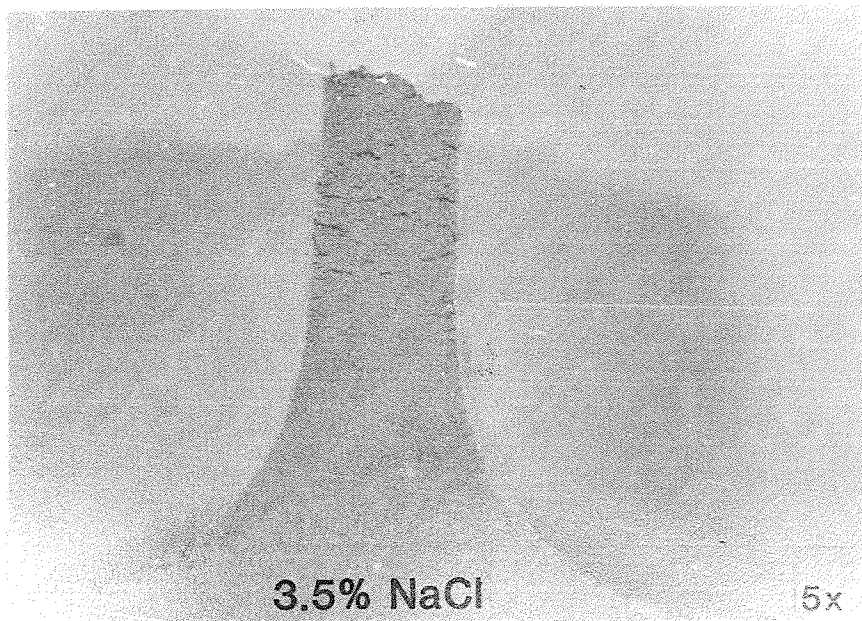
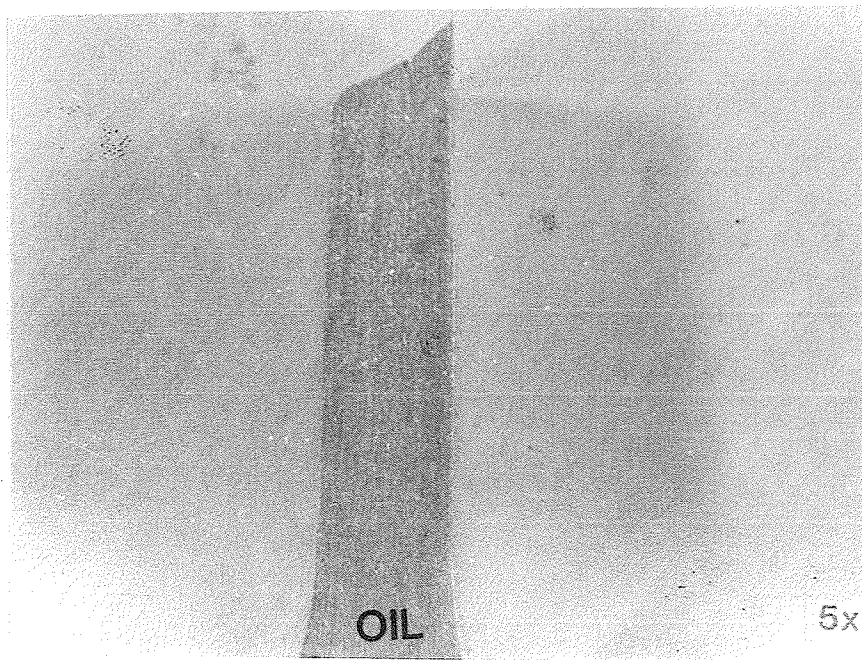


Figure 55. Slow strain-rate test specimens of alloy 5 air cooled from SHT and naturally aged for 16 hours. Tested in oil and 3.5% NaCl solution at $\dot{\epsilon}=4.1 \times 10^{-7} \text{ s}^{-1}$.

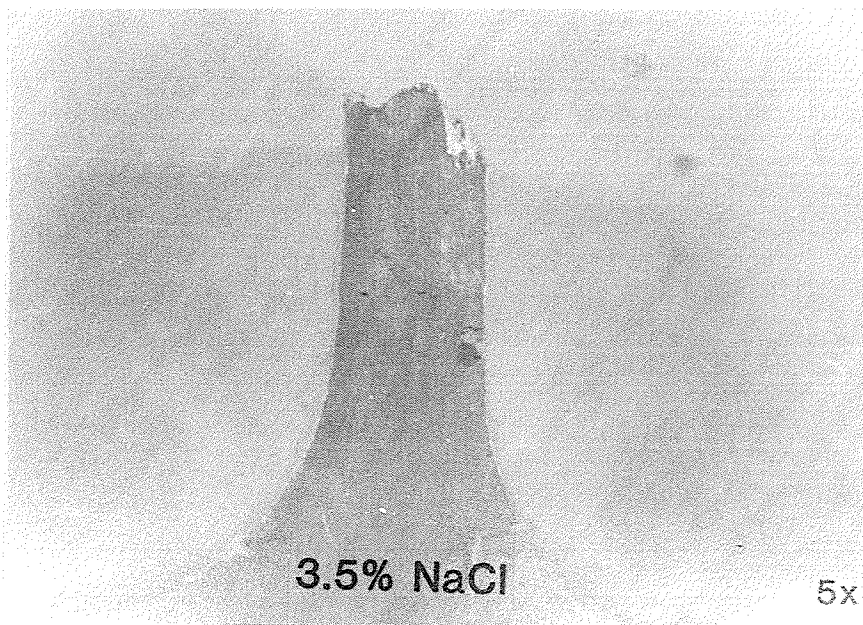
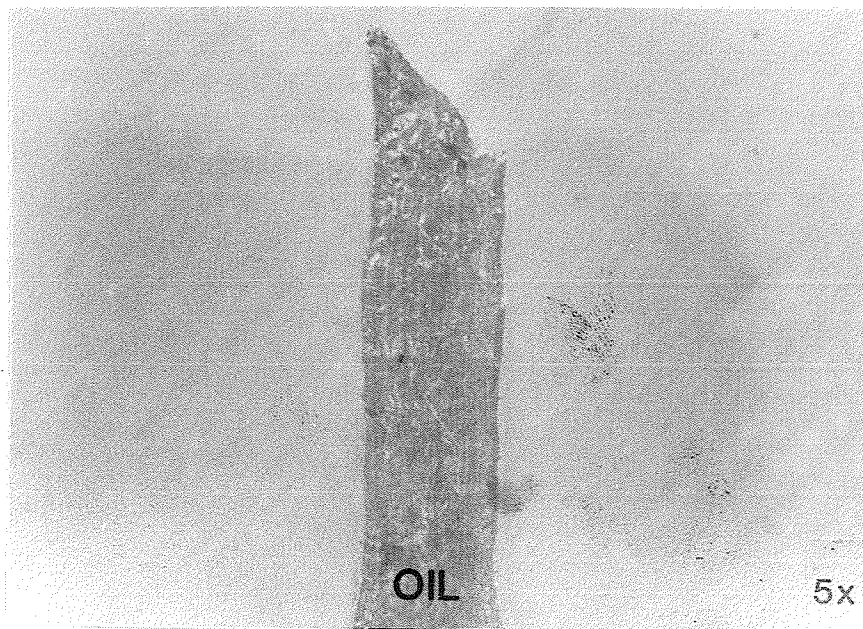


Figure 56. Slow strain-rate test specimens of alloy 4 air cooled in a block from SHT and naturally aged for 16 hours. Tested in oil and 3.5% NaCl solution at $\dot{\epsilon}=4.1 \times 10^{-7} \text{ s}^{-1}$.

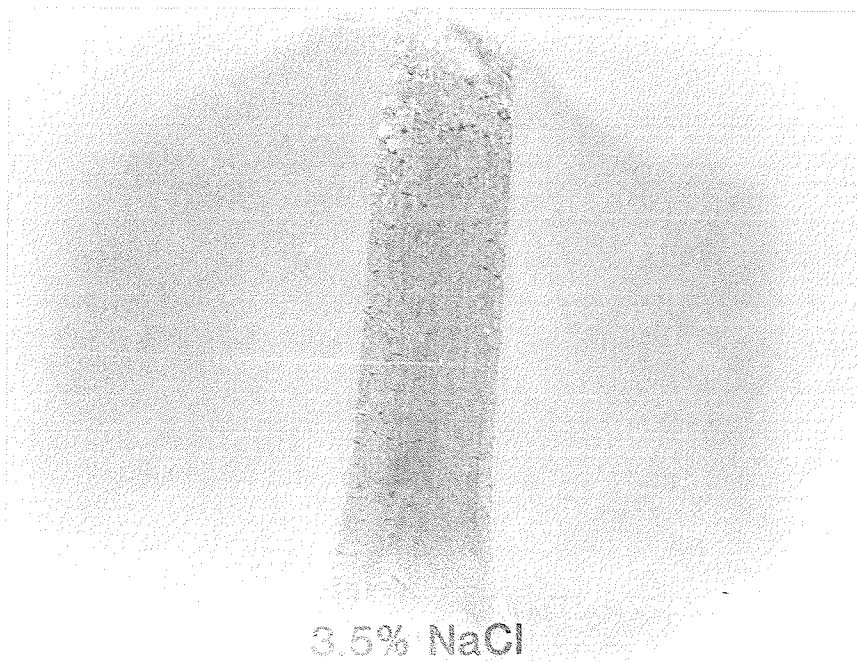
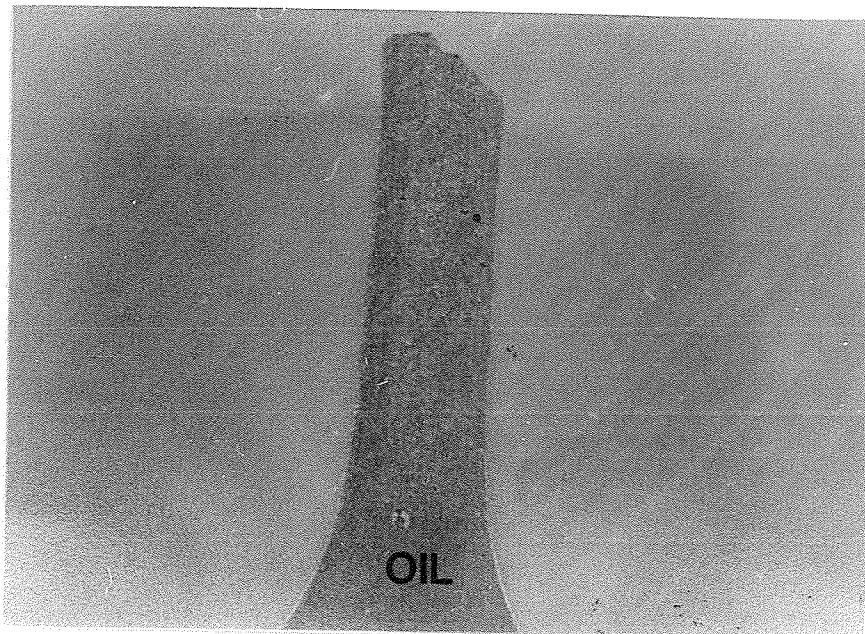
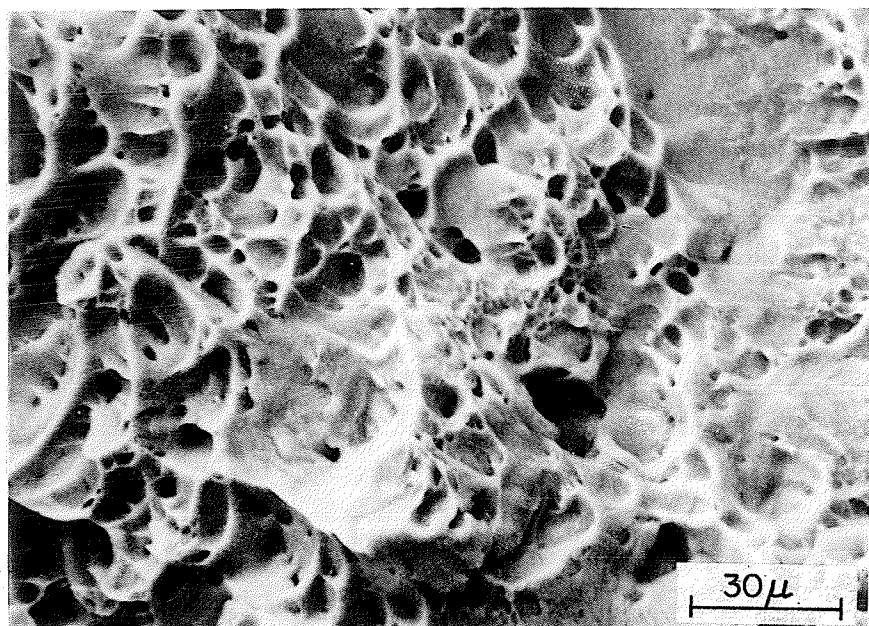
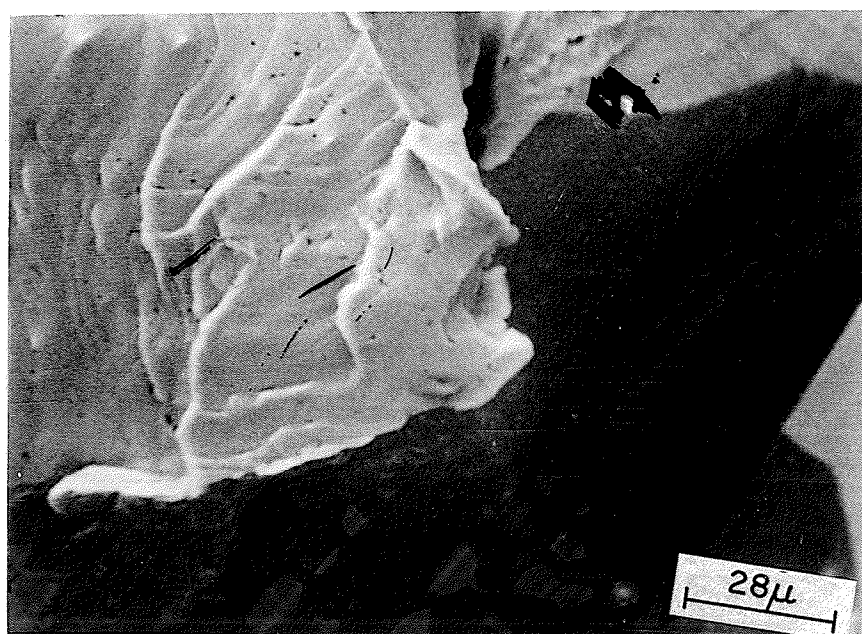


Figure 57. Slow strain-rate test specimens of alloy 5 air cooled in a block from SHT and naturally aged for 16 hours. Tested in oil and 3.5% NaCl solution at $\dot{\epsilon}=4.1 \times 10^{-7} \text{ s}^{-1}$.

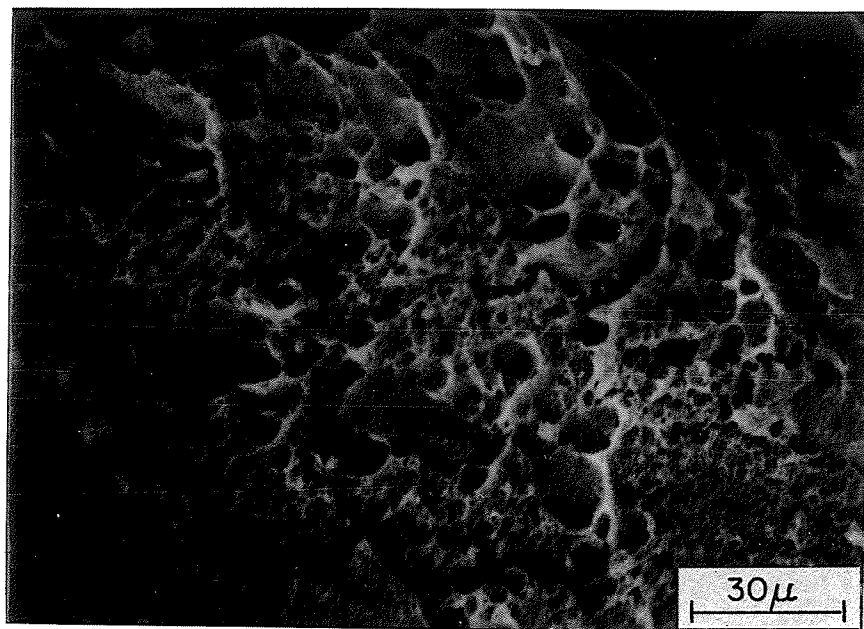


OIL

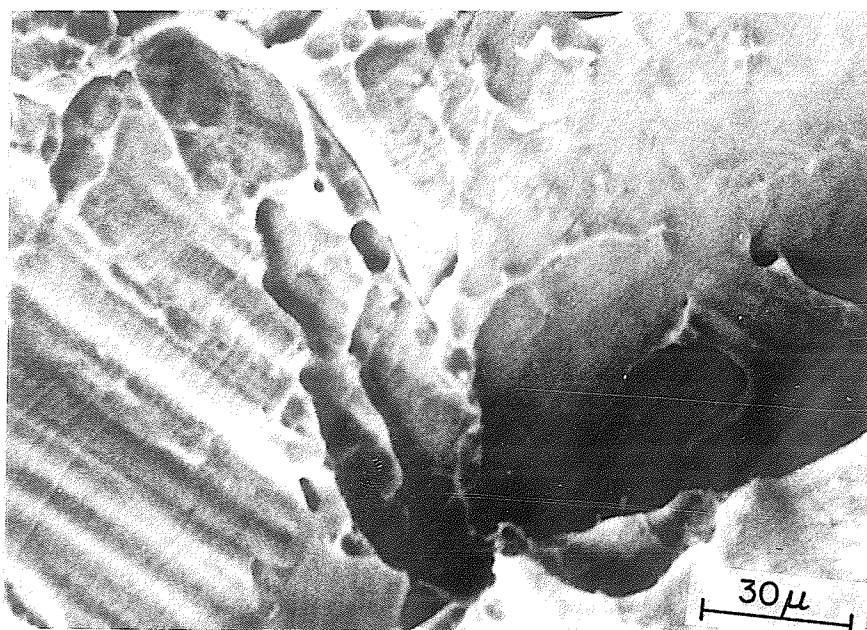


NaCl

Figure 58. SEM fracture surface photomicrographs of alloy 4 specimens water quenched from SHT and naturally aged for 16 hours. Tested in oil and 3.5% NaCl solution at $\dot{\epsilon}=4.1 \times 10^{-7} \text{ s}^{-1}$.

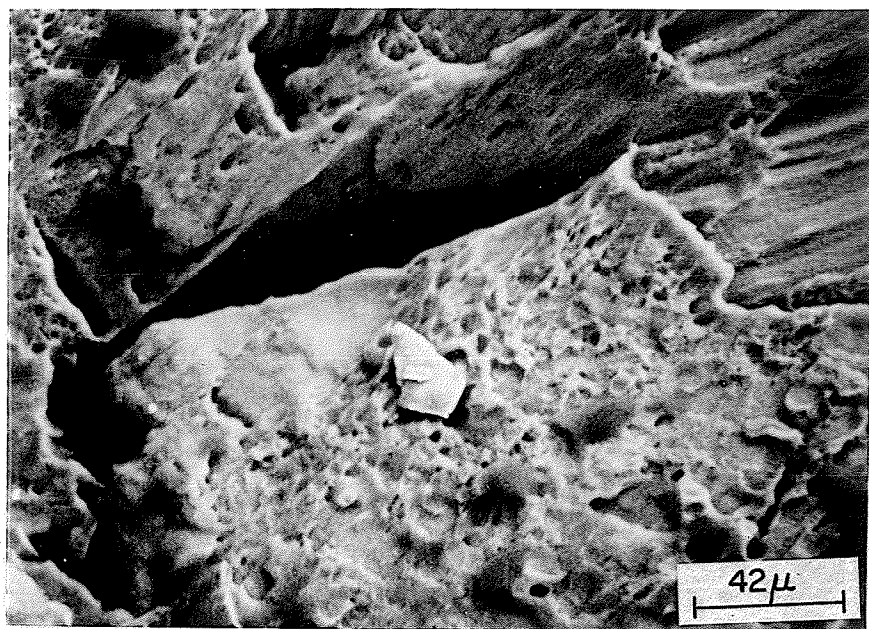


OIL

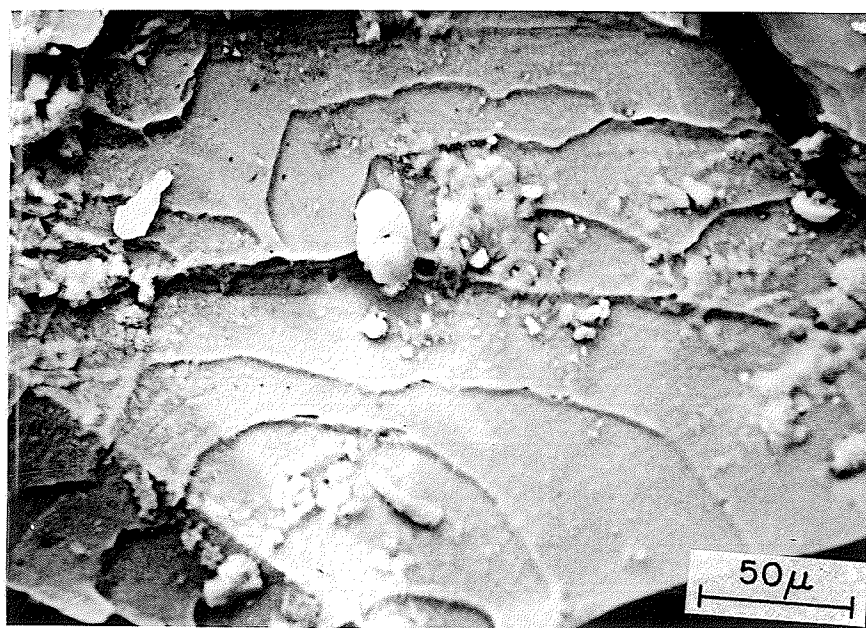


NaCl

Figure 59. SEM fracture surface photomicrographs of alloy 5 specimens water quenched from SHT and naturally aged for 16 hours. Tested in oil and 3.5% NaCl solution at $\dot{\epsilon}=4.1 \times 10^{-7} \text{ s}^{-1}$.

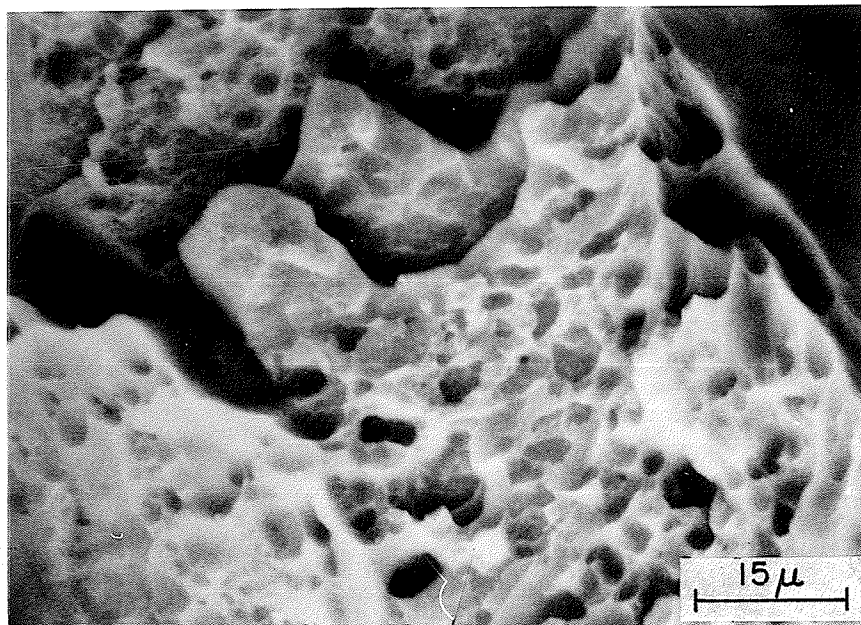


OIL



NaCl

Figure 60. SEM fracture surface photomicrographs of alloy 4 specimens air cooled from SHT and naturally aged for 16 hours. Tested in oil and 3.5% NaCl solution at $\dot{\epsilon}=4.1 \times 10^{-7} \text{ s}^{-1}$.

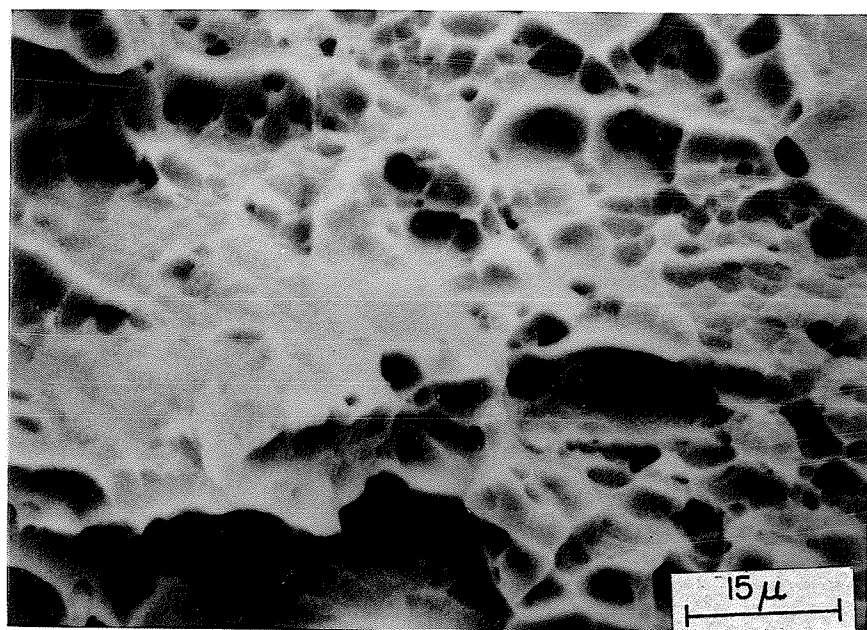


OIL

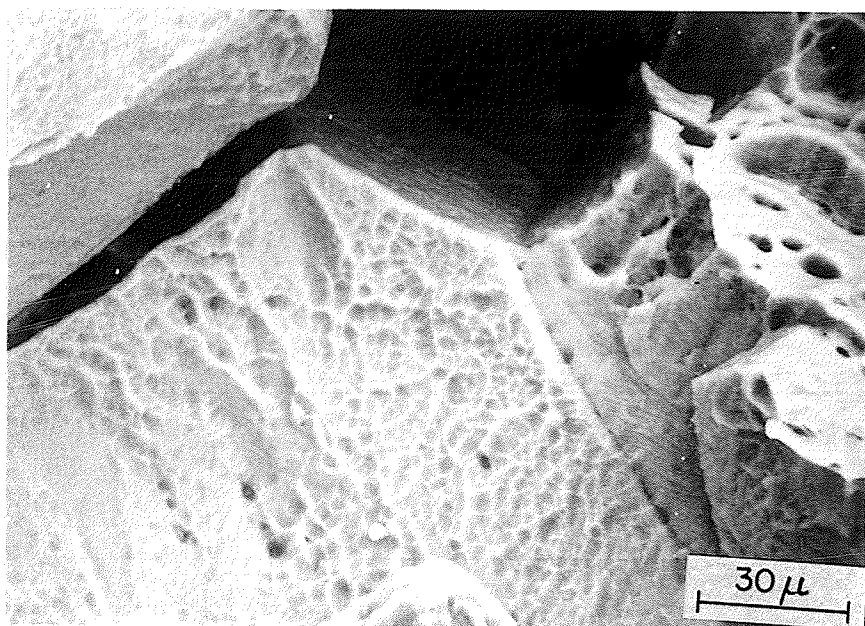


NaCl

Figure 61. SEM fracture surface photomicrographs of alloy 5 specimens air cooled from SHT and naturally aged for 16 hours. Tested in oil and 3.5% NaCl solution at $\dot{\epsilon}=4.1 \times 10^{-7} \text{ s}^{-1}$.

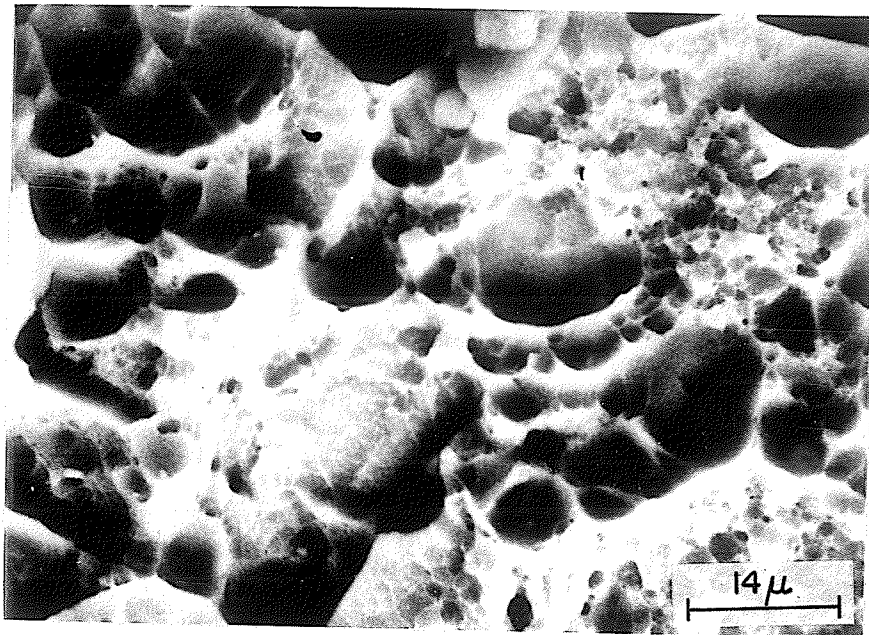


OIL

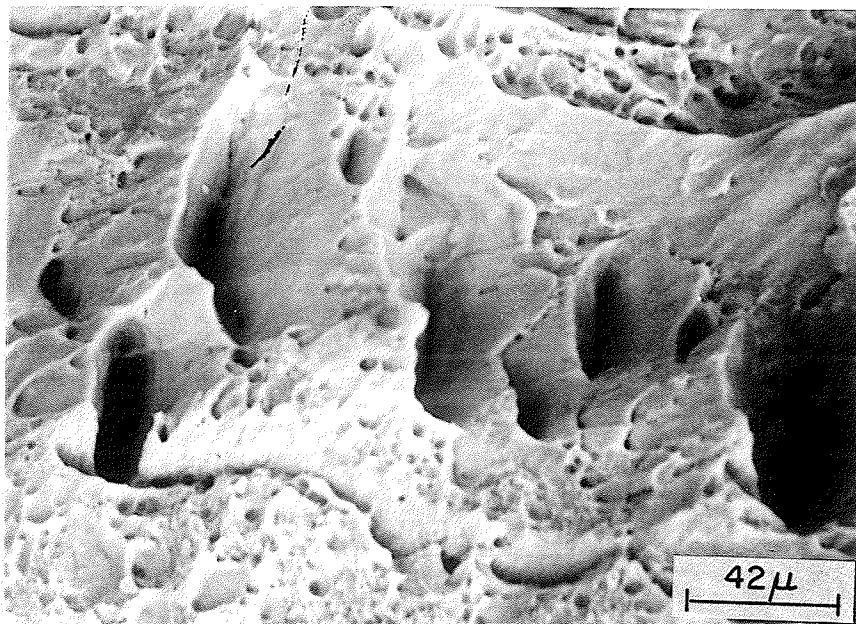


NaCl

Figure 62. SEM fracture surface photomicrographs of alloy 4 specimens air cooled in a block from SHT and naturally aged for 16 hours. Tested in oil and 3.5% NaCl solution at $\dot{\epsilon}=4.1 \times 10^{-7} \text{ s}^{-1}$.



OIL



NaCl

Figure 63. SEM fracture surface photomicrographs of alloy 5 specimens air cooled in a block from SHT and naturally aged for 16 hours. Tested in oil and 3.5% NaCl solution at $\dot{\epsilon}=4.1 \times 10^{-7} \text{ s}^{-1}$.

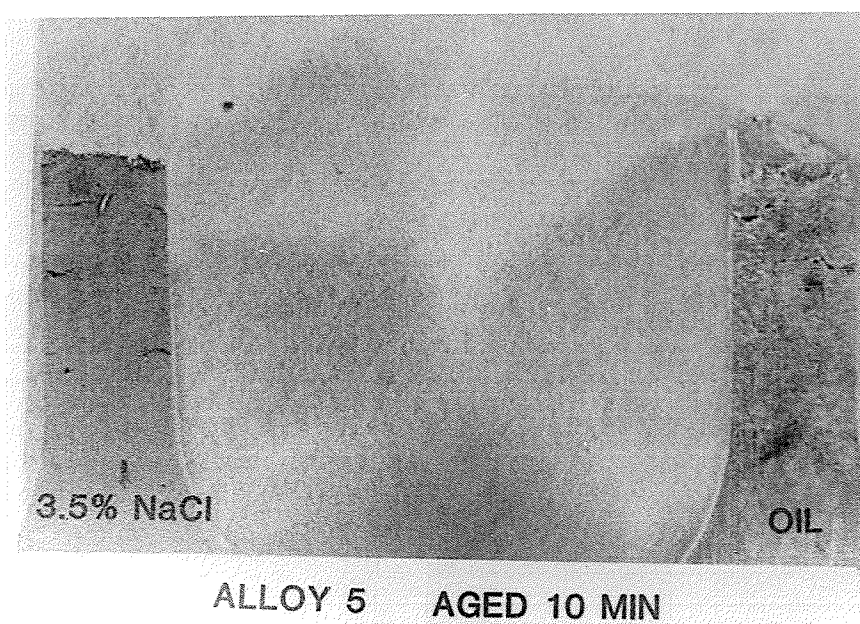
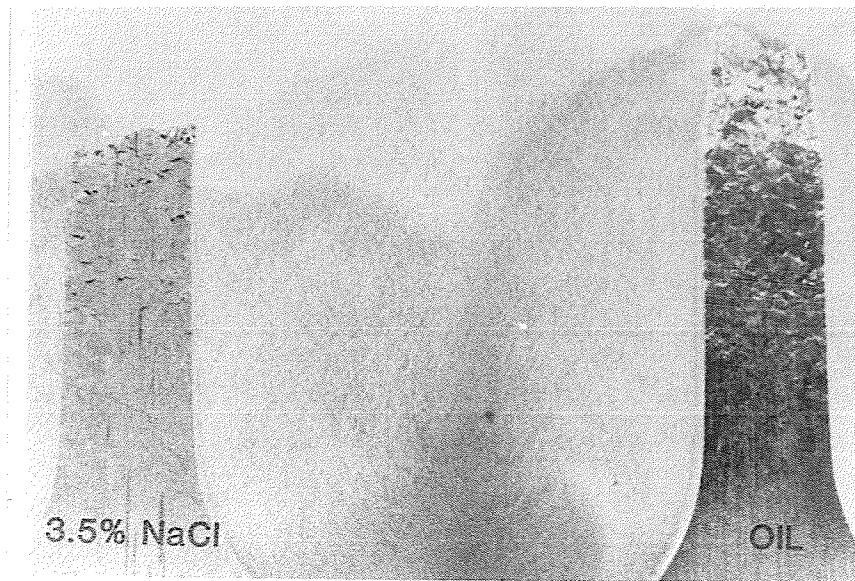
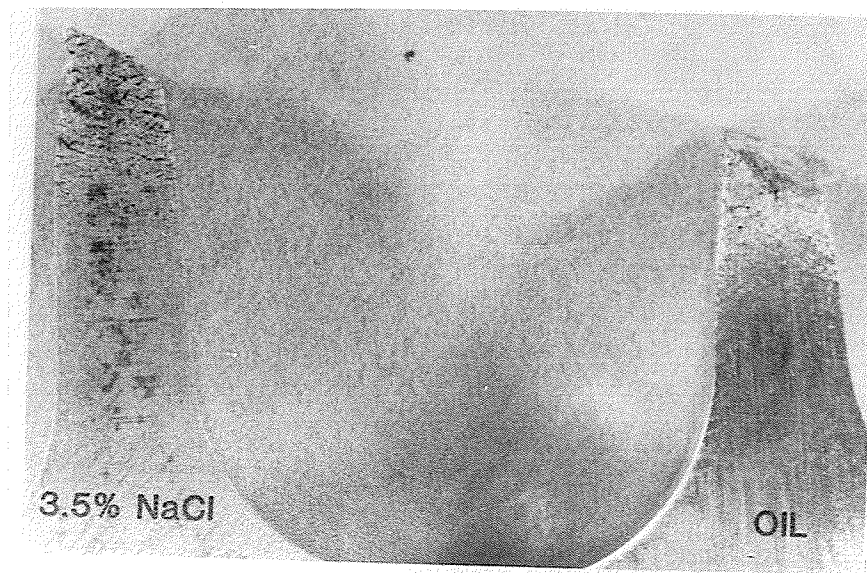


Figure 64. Slow strain-rate test specimens of alloys 4 and 5 water quenched from SHT, naturally aged for 16 hours and aged at 423K [150°C] for 10 minutes. Tested in oil and 3.5% NaCl solution at $\dot{\epsilon}=4.1 \times 10^{-7} \text{ s}^{-1}$.

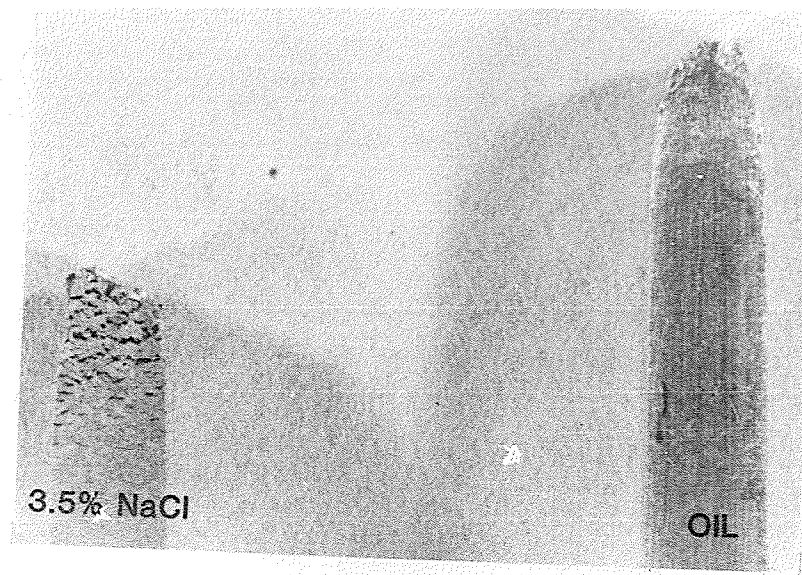


ALLOY 4 AGED 24 HOURS

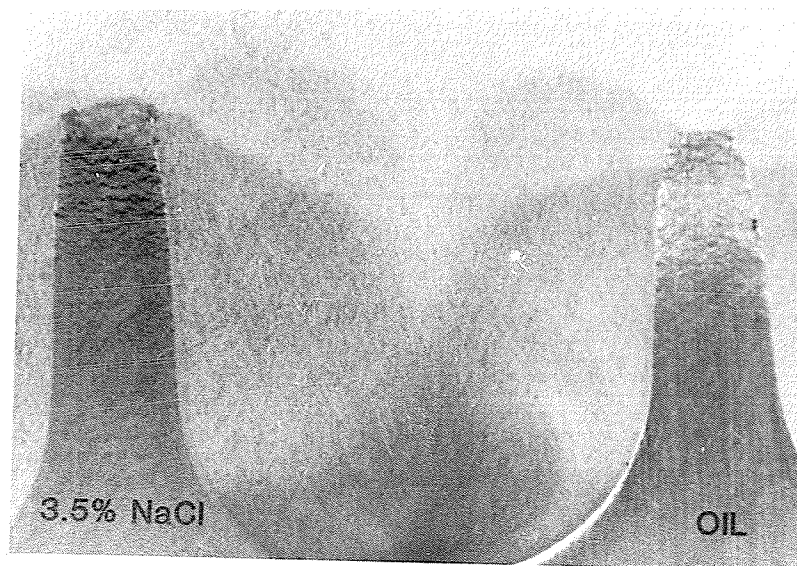


ALLOY 5 AGED 24 HOURS

Figure 65. Slow strain-rate test specimens of alloys 4 and 5 water quenched from SHT, naturally aged for 16 hours and aged at 423K [150°C] for 24 hours. Tested in oil and 3.5% NaCl solution at $\dot{\epsilon}=4.1 \times 10^{-7} \text{ s}^{-1}$.



ALLOY 4 AGED 1000 HOURS



ALLOY 5 AGED 1000 HOURS

Figure 66. Slow strain-rate test specimens of alloys 4 and 5 water quenched from SHT, naturally aged for 16 hours and aged at 423K [150°C] for 1000 hours. Tested in oil and 3.5% NaCl solution at $\dot{\epsilon}=4.1 \times 10^{-7} \text{ s}^{-1}$.

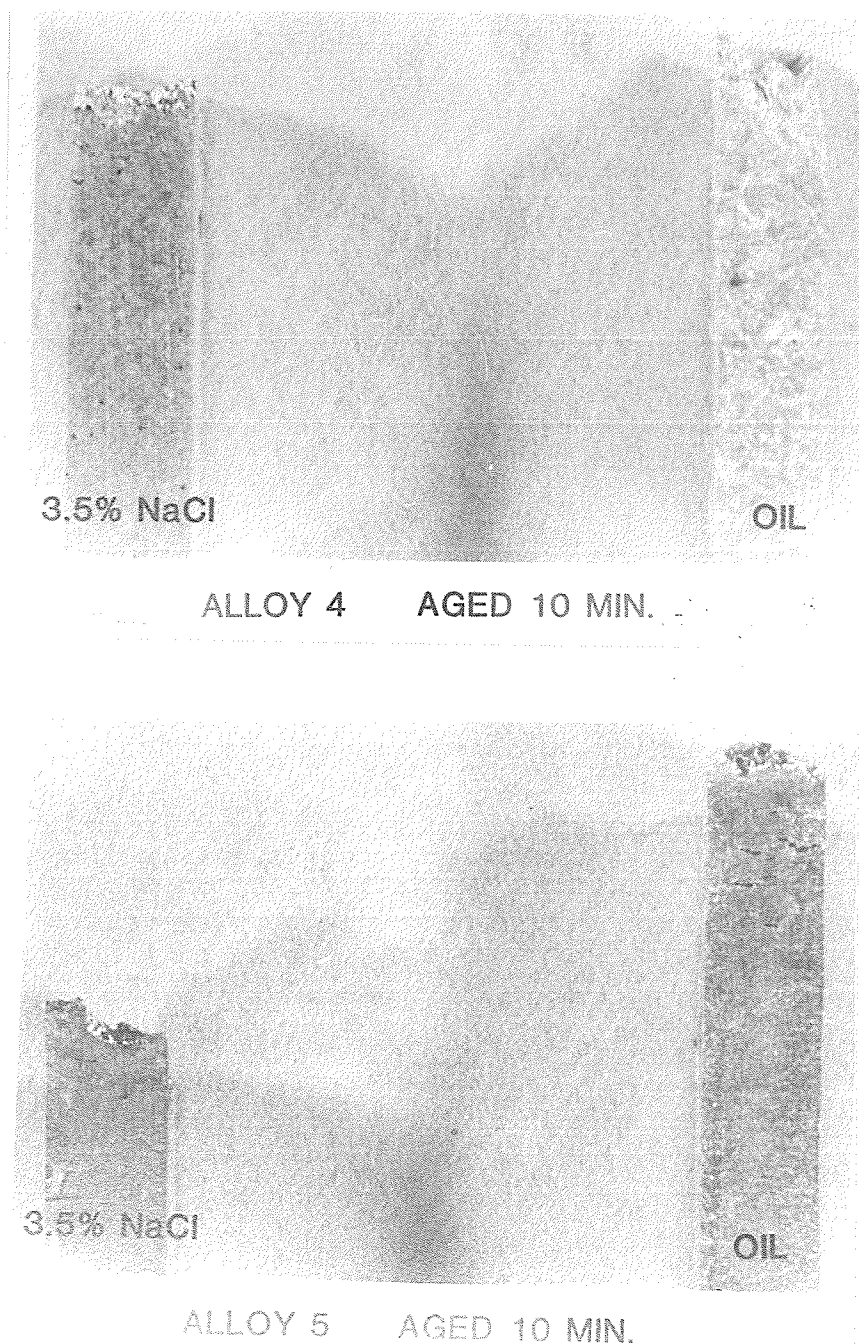


Figure 67. Slow strain-rate test specimens of alloys 4 and 5 water quenched from SHT, naturally aged for 16 hours and aged at 393K [120°C] for 10 minutes. Tested in oil and 3.5% NaCl solution at $\dot{\epsilon}=4.1 \times 10^{-7} \text{ s}^{-1}$.

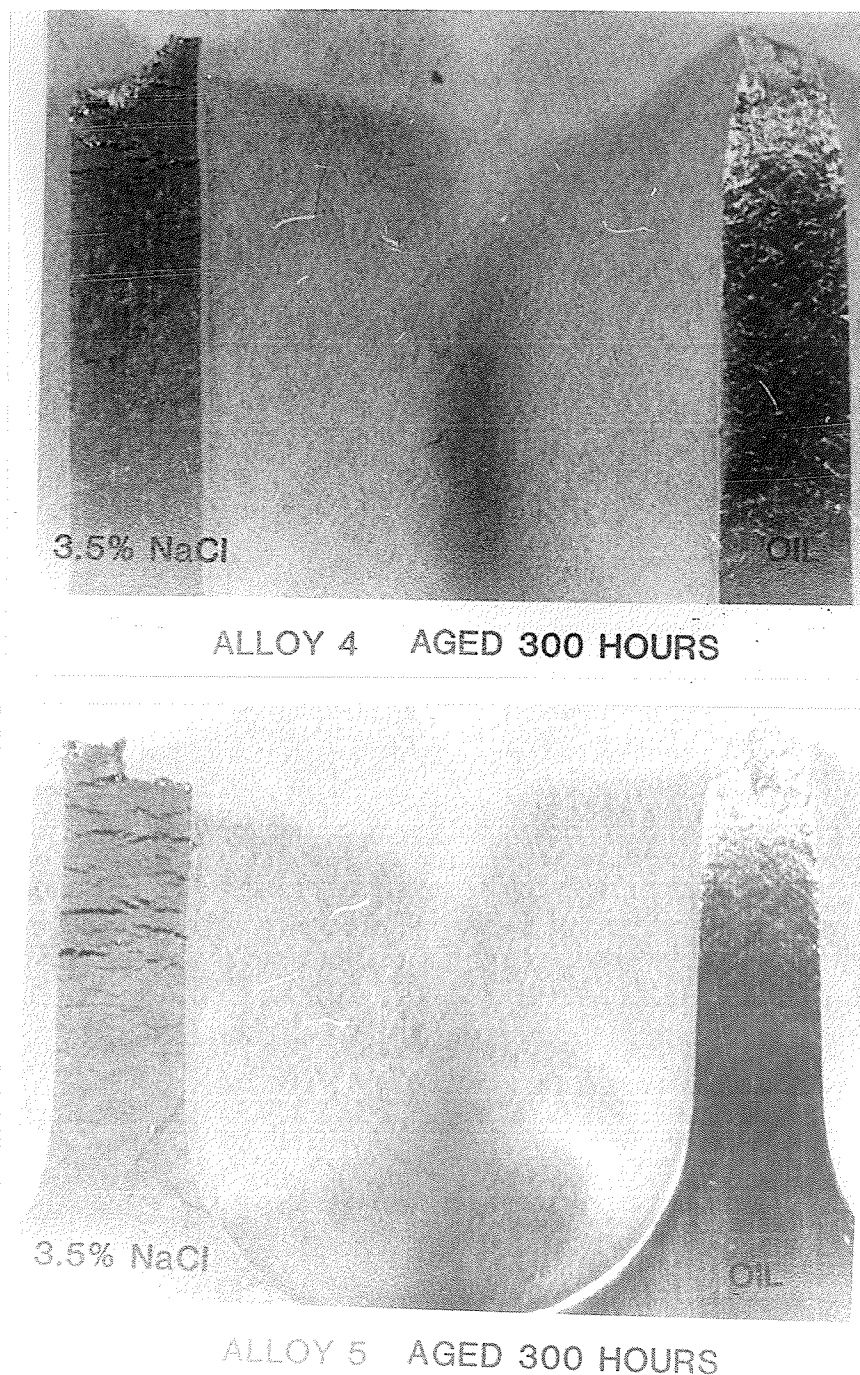
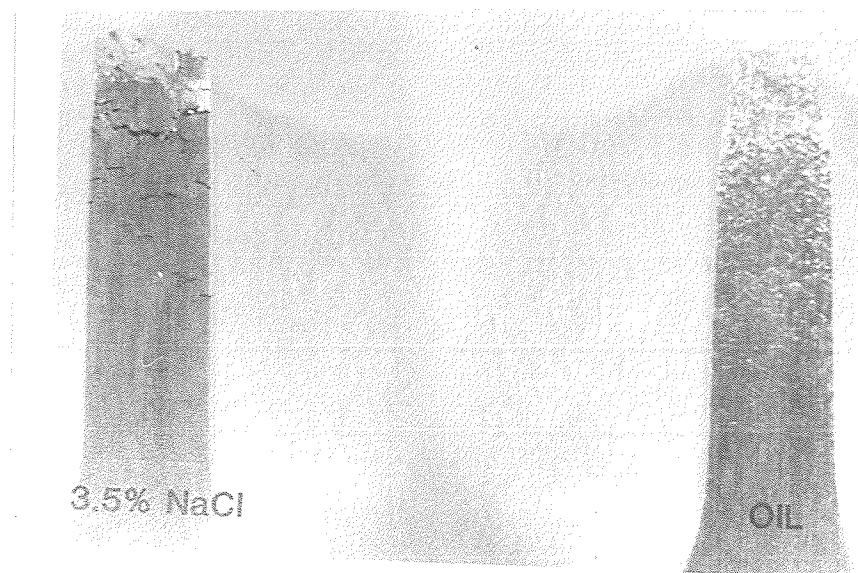
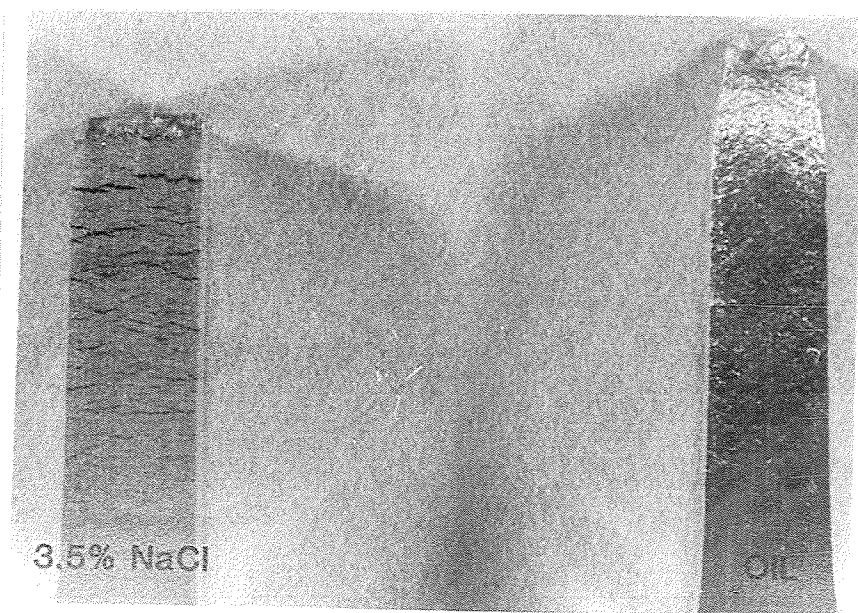


Figure 68. Slow strain-rate test specimens of alloys 4 and 5 water quenched from SHT, naturally aged for 16 hours and aged at 393K [120°C] for 300 hours. Tested in oil and 3.5% NaCl solution at $\dot{\epsilon}=4.1 \times 10^{-7} \text{ s}^{-1}$.



ALLOY 4 AGED 2000 HOURS



ALLOY 5 AGED 2000 HOURS

Figure 69. Slow strain-rate test specimens of alloys 4 and 5 water quenched from SHT, naturally aged for 16 hours and aged at 393K [120°C] for 2000 hours. Tested in oil and 3.5% NaCl solution at $\dot{\epsilon}=4.1 \times 10^{-7} \text{ s}^{-1}$.

CHAPTER 5 DISCUSSION

The experimental results of this investigation presented in Chapter 4 indicate that it is possible to achieve a satisfactory combination of mechanical properties and resistance to stress corrosion cracking of high purity AA7004 Al-Zn-Mg alloy by suitable thermal treatment and alloy additions. For example, AA7004 alloy containing zirconium exhibits a yield strength of 264.1 MPa, ultimate tensile strength of 315.6 MPa, 21.2% elongation to fracture, and maximum resistance to stress-corrosion cracking in a 3.5% NaCl solution as determined by using the slow strain-rate technique. These properties are obtained by solution heat treating the alloy at 773K [500°C] for 30 minutes, water quenching to room temperature followed by natural aging for 16 hours and subsequent artificial aging at 423K [150°C] for 24 hours.

In this chapter an attempt is made to relate the structure, the mechanical properties, and the stress corrosion cracking behavior of AA7004 aluminum alloy developed by various thermal treatments.

5.1. Aging Kinetics and Metallography

The optical microstructure of the zirconium-free alloy, alloy 4, consists of large, fully recrystallized grains. However, that of the zirconium-containing alloy, alloy 5, is non-recrystallized due to the well known recrystallization retarding effect of zirconium^(53,54) (Figure 12). The presence of zirconium induces the formation of small particles of intermetallic phases which retard recrystallization by preventing large angle grain boundaries from moving during solution heat treatment⁽⁶¹⁾.

Upon aging at either 423K [150°C] or 393K [120°C] following natural aging for 16 hours both the yield and ultimate tensile strength as well as the hardness of both alloys decrease in the first 10 minutes but they then start to increase (Figures 4,5,6,10 and 11). The initial drop in strength and hardness is likely due to dissolution of G.P. zones that formed during room temperature aging. This explanation is supported by the absence of the initial decrease when specimens were aged at 423K [150°C] without prior natural aging (Figures 7 to 9). This behaviour, which has also been observed by others⁽⁶²⁾, was verified by differential scanning calorimetry (Figures 32 and 33). The endothermic reaction observed upon heating after room temperature aging is likely due to dissolution or partial reversion of the G.P. zones which form during low temperature aging.

On further aging the hardness, yield and ultimate tensile strength of both alloys increase reaching a peak after 24 hours of aging at 423K [150°C] or 300 hours at 393K [120°C]. For example the yield strength of alloy 5 first decreased from 115 to 62 MPa after 10 minutes of aging at 423K [150°C] but then increased to 262 MPa after 24 hours of aging. The increase in strength is attributed to precipitation of the semi-coherent η' phase as observed in other Al-Zn-Mg alloys⁽³⁾. On overaging, η' transforms into the incoherent equilibrium η , MgZn_2 , phase⁽³⁾ resulting in a decrease in strength by affecting the precipitate-dislocation interaction which changes from shearing of precipitates by dislocation to bypassing them⁽⁶¹⁾.

5.2. Stress Corrosion Behaviour

The stress-corrosion cracking behaviour of the alloys used in this investigation was evaluated using the slow strain-rate technique. As described previously, samples are tensile tested at relatively slow strain-rates in corrosive and inert environments and parameters such as elongation to fracture or reduction in cross sectional area are compared in the two environments.

In the present investigation variously heat treated samples were tested in a 3.5wt% solution of NaCl and silicone oil at room temperature and at initial strain-rates between

4.1×10^{-7} and $4.1 \times 10^{-4} \text{s}^{-1}$. The susceptibility to stress-corrosion cracking for each heat treatment condition was then determined by comparing the total elongation to fracture in the two environments or the stress-corrosion cracking index, I_{SCC} . I_{SCC} is defined as the ratio of the total elongation to fracture of a sample tested in 3.5% NaCl solution and the total elongation to fracture of a sample tested in silicone oil, when both samples have identical compositions and microstructures and were tested at the same strain-rate and temperature.

SCC in Al-Zn-Mg alloys is invariably intergranular and, therefore, the grain boundary morphology has the greatest influence on the stress corrosion cracking behaviour of a given alloy. However, it has also been suggested that the precipitate distribution within the grains may also have an effect on this behaviour⁽³⁾. The main microstructural features that influence the SCC behaviour of these alloys are: grain morphology, the size and distribution of grain boundary precipitates, and the size or width of the precipitate free zones which develop around grain boundaries upon aging.

Although some disagreement among various investigators exists, it is generally believed that the stress corrosion cracking susceptibility of Al-Zn-Mg alloys is as follows:

1. is lower when the grains are non-recrystallized, i.e. they are pancake shaped rather than equiaxed.
2. decreases as the size and interparticle spacing of

the grain boundary precipitates increases, i.e. over-aged alloys.

3. decreases as the width of the precipitate-free zones around grain boundaries increases, although some investigators have not observed any influence ⁽⁶³⁾.

The results of this investigation show that the zirconium-containing alloy, alloy 5, is more resistant to SCC than the zirconium free alloy, alloy 4 (Figure 48), which is in agreement with published results of many investigations ⁽⁵³⁻⁵⁶⁾. The beneficial effect of zirconium is mainly attributed to the prevention of recrystallization during solution heat treatment. However, it has also been suggested that the beneficial effect of zirconium is due to the potential difference between grain boundary precipitates and the matrix being reduced by rendering the grain boundary precipitates less anodic ⁽⁵⁵⁾. Obviously this effect is more pronounced in systems for which the electrochemical dissolution is the operating mechanism.

5.2.1. SCC of Solution Heat Treated Alloys

The effect of cooling rate from solution heat treatment on stress corrosion cracking behaviour was determined by cooling samples of both alloys using various cooling methods resulting in three progressively slower cooling rates, and

testing at initial strain-rates between 4.1×10^{-7} and $4.1 \times 10^{-4} \text{s}^{-1}$ at room temperature. It was determined that after an incubation period of 16 hours at room temperature the slowly cooled samples were more resistant to stress corrosion cracking than the water quenched samples (Figures 34-47). This behaviour may be attributed to compositional differences; i.e. zinc and/or magnesium segregation around the grain boundary region which would result in a potential difference between grain boundaries and adjoining areas. Thus, water quenching which produces a greater vacancy concentration at the grain boundaries than slower cooling results in higher solute segregation at grain boundary regions and renders these alloys more susceptible to stress corrosion cracking by increasing crack propagation rates. It was observed by examining thin foils in the transmission electron microscope that the grain boundaries are free of precipitates after natural aging, (Figures 13-15). The behaviour described above was observed for the entire strain-rate range used in this investigation. However, the degree of susceptibility was more pronounced at the slowest strain-rate i.e. $4.1 \times 10^{-7} \text{s}^{-1}$, which also indicates that evaluation of resistance to stress corrosion cracking using this technique is influenced by the strain-rate used.

5.2.2. Effect of Artificial Aging on SCC

To determine the effect of artificial aging on the stress-corrosion cracking behaviour of the two alloys used in this investigation, slow strain-rate tests were performed using specimens aged for up to 1000 hours at 423K [150°C] or 2000 hours at 393K [120°C] following the three cooling rates mentioned earlier and also aged naturally for 16 hours. As shown in Figures 49 and 50, the behaviour of the two alloys tested is quite different after the foregoing treatments. For the zirconium-free alloy, alloy 4, peak aged specimens were less susceptible than solution heat treated specimens, except for the slowly cooled specimens. It was also observed that the cooling rate from the solution heat treatment temperature does not have any significant influence on the SCC susceptibility of the peak aged specimens which is contrary to the observation in other aluminum alloys. However, over-aged specimens are not susceptible to stress corrosion cracking as has been reported by others. In contrast to the behaviour of alloy 4, aging the zirconium containing alloy, alloy 5, to peak reduces its susceptibility to SCC. Also the susceptibility of peak aged and overaged specimens is nearly the same. Both of these results are contrary to the observations in other aluminum alloys as mentioned earlier.

Transmission electron microscopy was used to relate the microstructure produced after each thermal treatment to the

stress corrosion cracking behaviour of these alloys. The main difference between the zirconium-free and the zirconium-containing alloy was the degree of recrystallization as mentioned earlier. The rippled surface effect which was observed in air cooled and air cooled in a block samples could be due to coherency strain of G.P. zones, whereas this effect was not observed in the water quenched samples, (Figures 13-15). After 10 minutes of aging at either 423K [150°C] or 393K [120°C] grain boundary precipitates became noticeable in the air cooled and slowly cooled samples. These grew in size after 24 hours of aging at 423K [150°C] or 300 hours at 393K [120°C]. Also, grain boundary precipitates as well as precipitates in the grains were observed in the water quenched samples after this treatment. It was also observed that the precipitate free zones, PFZ, around grain boundaries were wider in the slowly cooled samples and in alloy 5 than in alloy 4. The width of the PFZ increased as the cooling rate from solution heat treatment decreased (Table 10), which is in agreement with results for other aluminum alloys⁽⁴⁾. Contrary to results of other investigations^(3, 5, 2) the width of the precipitate free zones was not affected by aging time, with the exception of slowly cooled alloy 5. The size of the grain boundary precipitates increased with aging time at 423K [150°C] and also increased as the cooling rate from solution heat treatment decreased.

The increased resistance to stress corrosion cracking of alloy 4 with aging time after peak strength for all three cooling rates from solution heat treatment may have been due to the increased size and interparticle spacing of grain boundary precipitates and also due to the increased width of the precipitate free zones. However, the I_{sc} of the same alloy for samples cooled at different rates from solution heat treatment and aged at peak strength is essentially constant at about 0.55. Therefore, it is concluded that overaging rather than reduced cooling rates from solution heat treatment aids the stress-corrosion cracking resistance of high purity AA7004 aluminum alloy with a fully recrystallized structure. This suggests that the size of the grain boundary precipitates has a greater influence on the stress corrosion cracking behaviour of this alloy than the width of the precipitate free zones.

The behaviour of artificially aged zirconium-containing alloy under stress corrosion conditions was quite different than that of the zirconium-free alloy. The susceptibility to stress-corrosion cracking, expressed by I_{sc} , in the peak strength as well as in the overaged condition remained essentially unchanged between 0.9 and 1.0 (Figure 50), even though the various cooling rates from solution heat treatment produced precipitate free zones of different widths and grain boundary precipitates of different sizes. This indicates that high purity AA7004 aluminum alloy with a non-re-

crystallized structure produced by additions of zirconium is not particularly susceptible to SCC when aged at 423K [150°C]. The results of this investigation are, therefore, in agreement with the published data of Doig and Edington⁽⁶⁴⁾ who determined for an aluminum alloy with similar composition, that the width of the precipitate free zones is not the controlling factor but that the solute depletion within the precipitate free zones determines susceptibility of aluminum alloys to stress-corrosion cracking.

5.2.3. Fracture Surface Observations of SC Failures

A selected number of specimens representing both alloys were examined by optical metallography and also in the scanning electron microscope after testing at an initial strain-rate of $4.1 \times 10^{-7} \text{s}^{-1}$. It was observed that samples tested in a 3.5% NaCl solution developed intergranular cracks which were perpendicular to the direction of load application. However, cracks were not observed in specimens tested in oil (Figures 52-57), indicating that the test environment is solely responsible for crack initiation. Also, specimens tested in a 3.5% NaCl solution exhibited brittle fracture, whereas those tested in oil failed in a ductile manner as shown in Figures 58-63.

CHAPTER 6 CONCLUSIONS

The following conclusions can be drawn from this investigation:

1. The size of grain boundary precipitates and the width of the precipitate free zones both increase as cooling rate from SHT decreases.

2. Upon aging at 423K [150°C], the grain boundary precipitates increase in size with aging time. However, the width of the precipitate free zones seems to remain unchanged upon aging.

3. The slow strain-rate test is a simple and efficient technique used to establish the SCC susceptibility of aluminum alloys.

4. Susceptibility of AA7004 to SCC is most pronounced at the slowest initial strain-rate used, i.e. $4.1 \times 10^{-7} \text{ s}^{-1}$.

5. Slow cooling rates from the solution heat treatment temperature and additions of zirconium aid the SCC resistance of this alloy in the naturally aged condition.

6. The cooling rate from SHT has no influence on the SCC susceptibility of material peak aged at 423K [150°C].

7. The SCC resistance of AA7004 aluminum alloy having a fully recrystallized structure is higher in the overaged condition than in the peak aged condition.

8. The degree of recrystallization is likely the most important parameter of those microstructural features influencing the SCC resistance of AA7004.

9. Aging at 423K [150°C] results in a higher SCC resistance than aging at 393K [120°C].

10. The peak tensile properties are inferior when the alloy is aged at 423K [150°C] than at 393K [120°C].

11. The stress corrosion resistance of 7004 aluminum alloy, having a fully recrystallized structure, increases as the size of grain boundary precipitate particles increases.

CHAPTER 7 SUGGESTIONS FOR FUTURE WORK

In view of the controversy regarding the mechanism by which stress corrosion cracking takes place in aluminum alloys it is recommended that the operating mechanism in AA7004 be investigated. The chemical composition of the grain boundary area should be determined and then large scale samples made. Following this, the potential difference between grain boundary precipitates and the precipitate free zone as well as the potential difference between the precipitate free zone and the matrix for various heat treatments should be measured.

The above investigation should provide information concerning whether or not an electrochemical dissolution mechanism is operating during stress corrosion cracking of AA7004 aluminum alloy.

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