EXPERIMENTAL CAST NICKEL SUPERALLOYS AND GAMMA-PRIME ALLOYS FOR HIGH TEMPERATURE APPLICATIONS IN GAS TURBINES

J. E. Restall

National Gas Turbine Establishment
Pyestock, Farnborough, Hants, UK

ABSTRACT

A study has been made of the relationships between the constitution, microstructure and selected mechanical properties of a series of experimental nickel-base casting alloys designed for high temperature creep resistance. The investigation started with a study of phase equilibria and selected mechanical properties of a model heat-resistant alloy whose high density precluded its use as turbine blading. Experimental variants were designed by systematically substituting titanium and niobium for tantalum, and molybdenum for tungsten in the parent alloy. From this work two alloys, designated R6 and R8, have shown particular promise with respect to high temperature creep-rupture strength combined with microstructural stability, thermal shock resistance and ability to withstand long-term exposure in high velocity corrosion rig tests.

General observations were that the tensile and creep-rupture properties at temperatures up to 1040°C were similar to those of the strongest commercial casting alloys. Unidirectional solidification (UDS) improved the elongation-at-fracture values and creep-rupture lifetime of all alloys tested but the level of improvement was dependent on alloy composition and test conditions. The best performance was shown by UDS R8 alloy which at 62 MPa/1100°C exhibited more than 40°C improvement in 100 hour creep-rupture life over MarM246 alloy.

A correlation was obtained between creep-rupture duration and solvus temperature of the gamma-prime precipitate. Regression equations were also developed relating creep-rupture properties to alloy hardness. No correlation was obtained between strength properties and lattice-parameter mismatch between the various matrices and gamma-prime phases.

A potentially interesting outcome of the phase equilibria studies has been the testing in bulk form of materials based on alloyed gamma-prime (Ni_3Al). Alloys have been developed that combine good mechanical properties with excellent oxidation resistance and which exhibit good compatibility with aluminide-type coatings.

Introduction

During the evolution of the gas turbine engine successive generations of nickel- and cobalt-base superalloys have been developed to meet the stringent property requirements of components used in the hot parts of the engine. These developments have reached the stage where cast nickel alloys are commercially available which offer approximately 300°C improvement in short term (100 h) creep-rupture strength over that of the simple nickel-chromium alloys of 30 years ago. This attainment, coupled with advances made in foundry technology and in the development of blade cooling techniques, has maintained the viability of superalloys as major engine structural materials in face of competition from more refractory metallic and ceramic materials. Although only marginal improvements in high temperature strength can be expected from the further development of new nickel superalloys even modest gains, say 10°C, can be used to advantage.

An experimental programme has been undertaken on the study of constitution, microstructure and mechanical properties of selected commercial and experimental nickel cast superalloys from which it was hoped to develop new materials with better specific strength (strength/density) and improved structural stability during long term exposure at high temperatures. The first part of the programme was designed to provide information on how different metallic elements alloy with the three principal phases found in the microstructure. Experimental variants were designed by systematically substituting titanium and niobium for tantalum, and molybdenum for tungsten in a model creep-resistant alloy where the high density ($\approx$9 Mg/m^3) precluded its use as turbine blading. Metallurgical observations were made on the factors governing the mechanical behaviour of the polycrystalline cast superalloys. Subsequently effort was directed towards the development of a group of alloys based on the compositions of the gamma-prime precipitates found in the microstructure of superalloys with the expectation of achieving useful levels of creep strength coupled with improved oxidation resistance, impact strength and fatigue resistance.

Alloy compositions

Cast nickel alloys were prepared by systematically replacing, in part or wholly, other elements for tantalum and tungsten in a creep-resistant superalloy selected from Reference 1. This alloy served as a useful model for studying the possibility of developing lighter alloys of comparable or better strength and which are not susceptible to the formation of embrittling, topologically close-packed phases, in the microstructure. The alloy is designated W37 in Table 1 and nominally contains three atomic percentage* each of tantalum and tungsten in addition to a "base" of 0.11 B, 0.7 C, 13.0 Al, 7.0 Cr, 10.0 Co, 0.07 Zr, balance 63.1 atomic per cent Ni. Using the reference method from the Seven Springs Conference[2] the average electron hole number for this and variant alloys is approximately 2.0. Variants were designed by making up to a total of three atomic percentage in each of the groups (Ti, Nb, Ta) and (Mo, W). Previous work[3,4,5] had shown that the Ti, Nb, Ta group partitioned in a similar way between the phases present in the superalloy microstructure; Mo and W also tended to act in a similar manner to each other. The alloy compositions produced about the same quantities of gamma-prime and carbides in the as-cast microstructures. In Table 1 the alloy series may be divided into five groups, the first headed by W37 and the others by W34, W43, W41 and R4. Alloys in the W37 group contain two element variants each at the three atomic percent level. The W34 group alloys contain three atomic percentage of either Mo or W with equal additions of two elements from the (Ti, Nb, Ta) group. W43 and R3 represent alloy groups in which similar elements are present in equivalent proportions. Alloys R4 to R11 represent a range of concentrations of Ti/Nb/Ta and Mo/W together; two alloys of particular interest in this group are designated R6 and R8 respectively.

*Unless otherwise indicated, compositions are reported in atomic percentage

TABLE 1

Chemical Composition* and lattice parameter data for cast superalloys

Conventional superalloy	Nominal composition					Lattice parameter Å of phases	
	Ti	Nb	Mo	Ta	W	Gamma	Gamma-prime
W37	-	-	-	3	3	3.591	3.586
W36	-	3	-	-	3	3.585	3.583
W44	-	-	3	3	-	3.592	3.584
W47	-	3	3	-	-	3.591	3.583
R1	3	-	3	-	-	3.585	3.577
W49	3	-	-	-	3	3.584	3.581
W34	-	1.5	-	1.5	3	3.588	3.586
W50	1.5	-	-	1.5	3	3.587	3.579
R13	1.5	1.5	-	-	3	3.593	3.582
R2	1.5	-	3	1.5	-	3.588	3.582
R14	1.5	1.5	3	-	-	3.592	3.581
R15	-	1.5	3	1.5	-	3.593	3.584
W43	-	1.5	1.5	1.5	1.5	3.583	3.583
R3	1.0	1.0	1.5	1.0	1.5	3.595	3.583
W41	-	-	1.5	3.0	1.5	3.585	3.585
R4	1.0	1.0	2.0	1.0	1.0	3.592	3.582
⋮							
R6	0.5	1.25	1.5	1.25	1.5	3.595	3.585
R8	1.25	0.5	1.5	1.25	1.5	3.593	3.583
⋮							
R11	2.0	0.5	2.0	0.5	1.0	3.590	3.580

Typical composition ranges of gamma-prime alloys explored (atomic percentage)

Group 1 Al 15.5-19.2, Cr 4.0, Co 7.0, Ta 3.6, W 0.9, C 0.25, B 0.06, Zr 0.05, Ni balance

Group 2 Al 16.1-18.0, Ti 1.2-1.8, Co 7.3-7.6, Nb 1.1-1.5, Mo 0.9, Ta 2.3, W 0.8, C 0.25, B 0.06, Zr 0.05, Ni balance

Group 3 Either of Groups 1 or 2 with addition of 0.5 atomic percent Hf

*Composition of conventional superalloys includes a "base" of 0.11 B-0.7C-13.0 Al-7.0 Cr-10 Co-0.07 Zr- bal. Ni (atomic percentage)

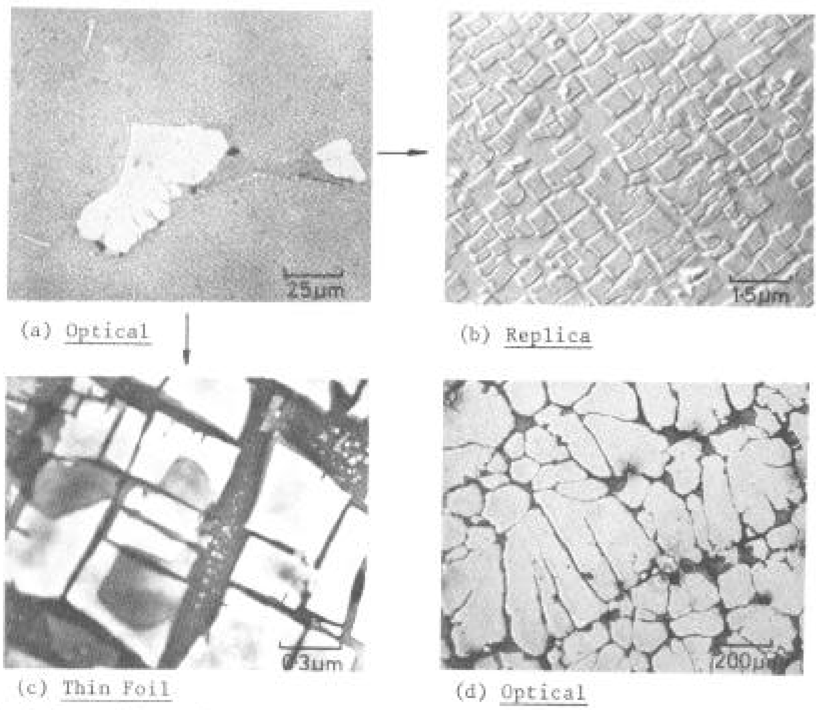
Also listed in Table 1 are the compositional ranges of selected gamma-prime alloys which have been developed from the phase equilibria studies on the conventional superalloys. Some of the gamma-prime alloys contain additions of hafnium. Further details of these γ' alloys are given in the patent literature.[6,7] Metallographic observations were also made on the microstructural stability of γ' alloys whose compositions were based on the analyses by Kriege and Baris[8] of precipitates in the commercial nickel superalloys IN100, Nimonic 115 and Nimocast 713.

Alloy preparation and testing

The alloys were prepared as 5 kg or 7 kg vacuum-melted ingots cast into 3 in. diameter steel moulds and the ingots re-melted and vacuum cast from about 1480°C into backed shell moulds preheated to 900°C. The mould assembly produced cylindrical blanks from which tensile, creep-rupture and other testpieces were machined. Some alloys were unidirectionally solidified (UDS) at a rate of 0.38 m h^{-1} (15 in. h^{-1}) using the modified Bridgman technique adopted by Northwood and Homewood[9]. The γ' alloys selected from Reference 8 were arc-melted to produce 50 g buttons which were then homogenised for 3 hours at 1270°C.

The conventional superalloys were examined by standard metallographic techniques in the as-cast condition and after 2000 hours heat-treatment at 850°C, and 200 hours at 1050°C. These temperatures are relevant to service use, 850°C being the region where tcp phases would be expected to be stable in some superalloys, and 1050°C where M_6C phases may be stable. Formation of eta carbide (M_6C) phases in the microstructure should be avoided as it involves the wastage of comparatively expensive and dense refractory metal elements such as molybdenum and tungsten. Compositions of the various phases were obtained from electron microprobe analysis, spectrographic and other chemical techniques and their structure from standard X-ray diffraction procedures[5].

The general metallographic features of the conventional nickel casting alloys were found to be very similar; examples are shown in Figure 1. The microstructure consists of primary dendrites of nickel solid solution (gamma) containing gamma-prime (Ni_3Al-type compound) precipitate, with interdendritic regions of primary MC carbide and areas of eutectic gamma-prime. Carbide particles which also generally contain some boron are also present at the boundaries and dispersed in the dendrites. Small amounts of borides and sulphides were detected in the interdendritic regions.



(a) Optical (b) Replica

(c) Thin Foil (d) Optical

Fig. 1 (a) to (c) optical and electron micrographs of cast superalloy R8
(d) gamma-prime alloy

After ageing treatments for 2000 h at 850°C only minor changes occurred in the microstructure. There was general break-up of the eutectic γ' and slight spheroidisation of the secondary γ', but there was no evidence of the characteristic Widmanstätten structure of sigma phase. Heat-treatment for 200 h at 1050°C produced coarsening of the secondary γ' and slight solutioning reaction of the MC phases. In contrast one sample of MarM246 alloy showed extensive precipitation of η carbide (M_6C).

Figure 1d shows the structure of an alloyed gamma-prime material composed essentially of a γ' dendrite with the interdendritic regions of lacy gamma residual structure. Microstructural details of the gamma-prime alloys were found to depend markedly on the aluminium content and at the 18/19 atomic percent aluminium level the γ' dendrites appear to form together with small amounts of β-NiAl and an infilling of $\gamma + \gamma'$.

To assess structural stability various γ' alloys were heat-treated for periods of up to 2000 h at temperatures in the range 800° to 1200°C. Subsequent metallographic examination showed that after ageing at 850°C the experimental γ' alloys were structurally stable whereas sigma phase precipitates were identified in the microstructure of both Nimonic 115-type γ' and IN100-type γ' alloys. No significant changes occurred in the experimental γ' alloys during long term exposure at temperatures up to 1000°C, and even at 1200°C only slight coalescence of the β-NiAl and γ phase occurred.

The various chemical and microprobe analysis data showed that Ti, Nb and Ta form MC phases and also alloy preferentially with the γ' phases, whereas Cr, Co, Mo and W alloy preferentially with the matrix phases. These analyses showed general trends for change in composition of the matrices with heat-treatment i.e. increases in the Al content and decrease in Co and Cr level associated with partial dissolution of gamma-prime and MC phases.

X-ray diffraction analyses confirmed that the experimental alloys were structurally stable during exposure at 850°C, and no significant precipitation of M_6C was observed after exposure at 1050°C. Very small differences were observed in lattice parameter between the various matrix and gamma-prime phases; data are included in Table 1.

Mechanical properties

The short term creep-rupture properties of the experimental alloys were measured at three selected test conditions. Hardness and miniature Charpy impact tests were done before and after heat-treatments at 850°C and 1000°C. Comparison creep tests were performed where appropriate on commercial materials. After this initial assessment two promising alloys, R6 and R8 with a density of 8.4 Mg/m^3, were subjected to a more-comprehensive assessment of mechanical properties. Factors governing the creep and short term tensile behaviour of the conventional alloys i.e. coherency strain, stability of the gamma-prime precipitate and general microstructural features were explored.

The experimental alloys were designed to be stable on thermal exposure and impact tests confirmed that this was so. Tests were done on plain testpieces 6 cm length × 7.2 mm diameter and on miniature Charpy testpieces that were cast to the finished size of 4.3 cm × 2.8 mm sq. In the as-cast condition the impact strength values of the experimental alloys were typical of those for commercial cast nickel superalloys currently used in gas turbines. The miniature Charpy data were typically in the range 1.3 to 5.2 Joules with a few in excess of these values for the alloys in the cast condition, or after heat-treatments for 2000 h at 850°C, or 200 h at 1050°C. Some samples of Nimonic 115 alloy manufactured when control of composition by PHACOMP was not employed were shown to be structurally unstable. Sigma phase precipitates caused significant embrittlement with fracture energies being reduced by an order of magnitude i.e. to approximately 0.14 J compared with a minimum of 11 J for samples with a similar history but free of sigma phase. The larger sized testpieces in alloys R6 and R8 had fracture energies in the range 20 J to 28 J in the conventionally cast conditions. Unidirectional solidification improved these values up to 34 J as-solidified, and after 200 h exposure at 1050°C the fracture energy values increased to the range 52 J to 60 J. The experimental gamma-prime alloys displayed similar levels of toughness to those of the conventional nickel casting alloys.

The tensile properties of the experimental alloys R6 and R8 were similar to those of commercial high strength casting alloys, with 0.2 per cent proof stress values in the range 750 MPa to 870 MPa, (109 to 126 ksi) and fracture stresses from 980 MPa to 1090 MPa (142 to 158 ksi) at room temperature. Unidirectional solidification improved the ductility of the experimental casting alloys. The tensile properties of the experimental gamma-prime alloys were similar to those of the conventional nickel superalloys, and the usual benefits accrued from unidirectional solidification.

Creep-rupture tests were performed on the whole group of casting alloys at 850°C, 1000°C and 1040°C. Additional tests were done on the two alloys R6 and R8 at 750/760°C and at higher temperatures in the range 1100° to 1200°C. Comparison was made between selected experimental and commercial alloys in both the conventionally-cast and UDS condition. The general observations were that the creep-rupture properties of the experimental alloys at temperatures up to 1040°C were similar to those of the high strength commercial casting alloys. UDS improved the elongation-at-fracture values and creep-rupture lifetime of all alloys tested but the level of improvement was found to be dependent on alloy composition and test conditions. The best performance among the experimental alloys was shown by UDS R8 alloy which at 62 MPa/1100°C (9 ksi/2012°F) exhibited more than 40°C improvement for a 100 h rupture life over MarM246 alloy. A summary of the creep-rupture properties of selected alloys is listed in Table 2. Laboratory test data for R6 and R8 are also shown on the Larson-Miller diagram, Figure 2a. The creep-rupture properties of the experimental gamma-prime alloys matched those of commercial superalloys.

TABLE 2

Temperature °C to produce rupture in 100 h* for conventional nickel superalloys and a gamma-prime type alloy

Stress, MPa	Alloy/Condition	R6	R8	IN100	MarM246	γ' alloy
463	Conventionally cast	855	848	831	839	842
	UDS	860	865	845	863	855
108	Conventionally cast	1056	1055	1036	1046	1010
	UDS	1058	1066	1041	1064	1040
62	Conventionally cast	1110	1112	NA	1085	1070
	UDS	1136	1147	1070	1101	1121

*Data based on Larson-Miller parameter $P = T[20 + \log t]$ where T = temperature K, t = meantime to rupture. No correction has been allowed for alloy density which would otherwise increase temperatures for IN100 alloy by about 40°C at 463 MPa and 18°C at 108 MPa.

NA - rupture duration too short (2 h) for meaningful extrapolation.

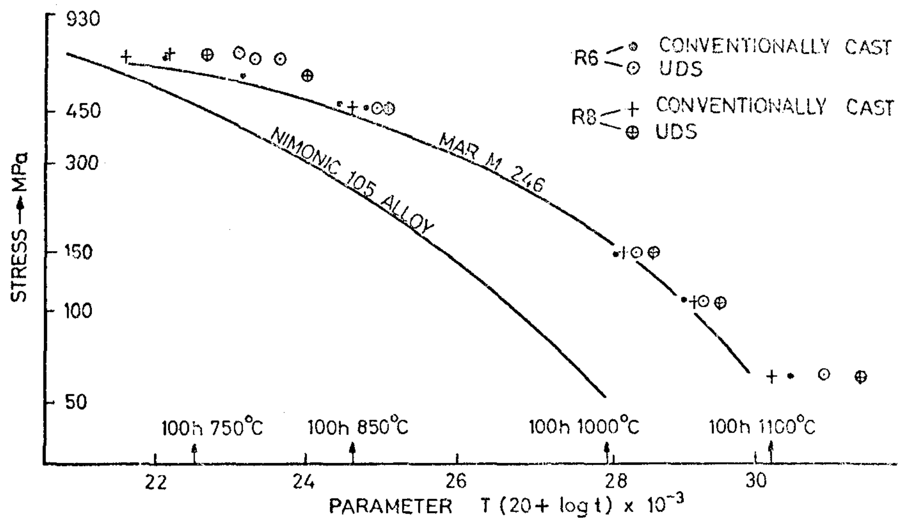


FIG.2 (a) STRESS-RUPTURE PROPERTIES OF NICKEL SUPERALLOYS

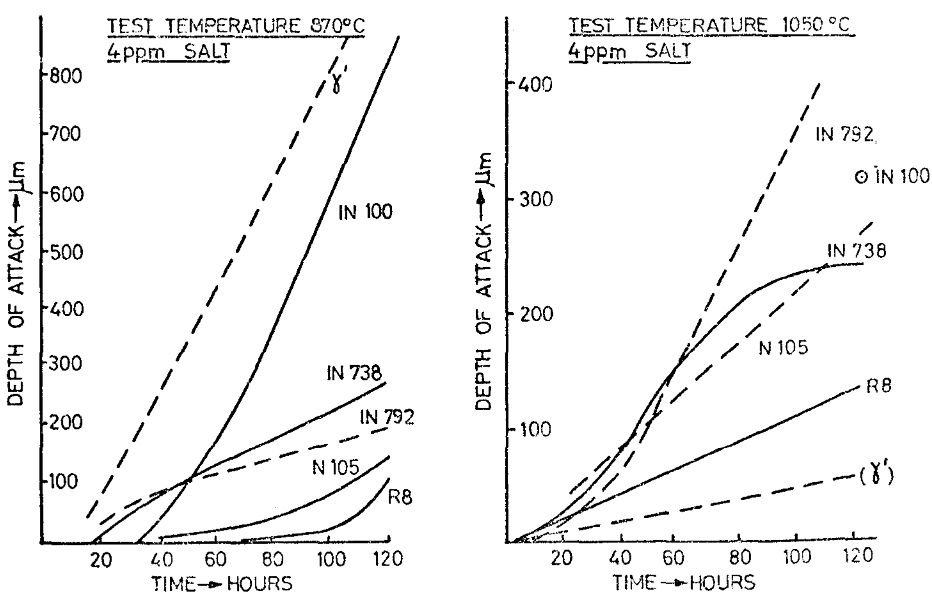


FIG.2 (b) SULPHIDATION-CORROSION TEST DATA

TABLE 3

Linear regression equations for creep-rupture tests on conventionally-cast alloys at 850°C, 1000°C and 1040°C

The equations are of the form $y = A + Bx$, where A and B are coefficients, y is the rupture life (hours) and the variable x is either the γ' solvus temperature (°C) or mean level of 'as-cast' hardness (DPN).

Test conditions	x	A	B	% Significance	Standard deviation (hours)
463 MPa/850°C	γ' solvus	-1893.6	1.6233	99.0	36.0
"	DPN	-411.6	1.2677	99.0	36.5
154 MPa/1000°C	γ' solvus	-2487.9	2.1484	99.9	41.3
"	DPN	-619.8	1.9257	99.9	37.0
108 MPa/1040°C	γ' solvus	-2515.5	2.1956	99.9	35.8
"	DPN	-339.5	1.2595	95.0	44.2

Metallurgical observations were made on the factors influencing the mechanical behaviour of the experimental nickel casting alloys, i.e. compositional effects, coherency strain and volume fraction of γ'. No correlation was obtained between creep-rupture properties and mismatch in lattice parameter between the matrix and γ' phases, whereas the solvus temperature of the γ' precipitate and alloy hardness could be correlated with creep resistance. Regression equations describing these relationships are listed in Table 3; more details are given in Reference 5.

Mechanical fatigue and thermal fatigue tests were done on the two superalloys R6 and R8, and selected gamma-prime alloys. Rotating bend tests at room temperature and 750°C (1382°F) showed the fatigue performance of these materials to be in the range typical of commercial casting alloys. Thermal fatigue resistance was determined using the fluidised bed testing procedure developed at NGTE in which taper disc specimens were cycled between room temperature and a maximum temperature of 970°C, 1070°C and 1120°C (1778 to 2048°F) respectively. The number of cycles to the onset of cracking was taken as a measure of thermal fatigue resistance. For any of these test conditions the performance of R6, R8 and the gamma-prime alloys were at least as good as those for other high strength casting alloys.

Oxidation and corrosion behaviour

Oxidation tests were done in laboratory furnaces at temperatures up to 1100°C (2012°F). Under cyclic oxidation conditions in which testpieces were cooled to room temperature at intervals of 20 h in a total duration of 100 h the oxidation resistance of R6 and R8 was better than that of some commercial superalloys. The cyclic oxidation behaviour of the experimental γ' alloys was considerably superior to that of any superalloy tested, and there was no evidence of preferential grain boundary attack (pest) which is encountered in some intermetallic compounds such as aluminium rich β-NiAl.

Dynamic sulphidation-corrosion tests were carried out on R8 as a representative conventional superalloy, and a gamma-prime type alloy. In these tests bar testpieces were rotated at the periphery of a cage that was stationed in the centre of the hot gas stream generated by an aero engine type combustor. The salt burden of the hot gas stream was 4 ppm. Tests were done for times up to 120 h at metal temperatures of 870°C and 1050°C respectively (1598 and 1922°F).

Figure 2b illustrates the test data. Despite its comparatively low chromium content R8 gave a good performance. The gamma-prime type alloy with an even lower chromium content did not exhibit high corrosion resistance at 870°C but at 1050°C it was the most oxidation resistant material tested.

Coating trials using pack-aluminising have been done on R6, R8 and gamma-prime alloys without detriment to their mechanical properties. Aluminide coatings improved the thermal fatigue resistance of all materials tested, and under laboratory oxidation test conditions it was found that part of the coating survived on the surface of γ' alloys even after 1000 h exposure at 1200°C (2192°F), whereas similar coatings on conventional superalloys were consumed by diffusion degradation at 1050°C. It would appear that the aluminium content of the substrate has a marked effect on the rate at which aluminide coatings degrade, as the temperature capability of a 19 at % Al alloy was clearly higher than that of a similar alloy containing only 15 at % Al.

Summary

The relationships between the constitution, microstructure and selected mechanical properties of creep-resistant cast nickel alloys have been explored. Among the experimental alloys two, designated R6 and R8, have excellent high temperature creep strength, structural stability, thermal shock resistance and hot corrosion resistance. Metallurgical observations on the factors governing the strength of these alloys suggested that the solvus temperature of the γ' precipitate and the alloy hardness could be related with creep-rupture properties. The information from the phase equilibria studies was used as a basis for developing gamma-prime base alloys that also combine good mechanical properties with very good oxidation resistance.

Acknowledgement

The author wishes to thank his colleagues Mr. M. J. Weaver for helpful discussion and providing some information on γ' alloys, and Mr. E. C. Toulson for experimental assistance.

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