GAS TURBINE BLADE ALLOYS

BY

J. E. RESTALL, B.SC., PH.D., C.ENG., M.I.M. (Royal Aircraft Establishment, Pyestock)

Summary

A brief account is presented of developments in high temperature nickel and cobalt alloys (superalloys) that are used for the manufacture of aerofoil components in aero and marine gas turbine engines. Over the last 40 years very many new materials have been developed, based, at least partly, on evolving understanding of the factors controlling strength, ductility, and hot corrosion behaviour. More recently a greater emphasis has been placed on developing manufacturing processes that can control the internal structure of aerofoil components and thus achieve still better properties and performance. Research into these areas has been triggered by the demands of both the makers and users of aero-engines; parallel work directed towards improving marine propulsion units has been small by comparison. Nevertheless, significant progress has been made and the possibilities for further 'spin-off' are indicated.

The specialized subject of protective coatings for use in marine gas turbines will be the subject of a later article.

INTRODUCTION

More than forty years have elapsed since the gas turbine engine established its position as a commonplace power plant for aircraft propulsion. In the intervening time the gas turbine has demonstrated its versatility by becoming adopted as the prime power unit in a wide variety of aero, industrial, and marine propulsion systems. During this time the power range, specific thrust, fuel efficiency, performance, reliability, and life have shown noticeable improvements due to operating at increased compressor ratios coupled with marked increases in the turbine operating temperature. These advances have been achieved through improvements in engineering design, the development of better materials, and improvements in the process technology employed for the manufacture of components.

Every component utilized for the construction of the gas turbine requires careful consideration with respect to the selection of materials from the viewpoint of both technical and economic considerations, and some compromise is inevitable. However, the most critical components that are primarily responsible for determining the design and operational life of advanced aero and marine engines are the first- and second-stage high pressure turbine rotor blades. Ideally, the materials employed for these components should possess good strength to weight ratio, adequate resistance to steady state and vibratory stress, toughness, and microstructural stability, etc., combined with resistance to environmental degradation by high temperature oxidation, corrosion, and erosion processes. Although they are not subject to such high levels of mechanical stress, the nozzle guide vanes may be subjected to even more severe environmental degradation than the rotor blades. This is because the NGV is the first turbine component to meet the combustion gas stream and is subject to higher temperature (i.e. up to 100 K higher), more severe transient thermal stresses and more active chemical environment than the first stage rotor blades. Environmental aspects are complicated, the main factors being a high temperature, high velocity gas stream with a marked non-uniformity of temperature, the presence of impurities arising from the intake air and the fuel and, depending on the combustor design, the possible presence of carbon particles.

During the early days of gas turbine development considerable attention was devoted to the possibility of using a wide range of fuels including the cheaper forms. It quickly became evident that the presence of residual impurities (sodium, vanadium, etc.) in certain fuels could generate major environmental problems for critical engine components through corrosion, fouling, and erosion. The immediate problems were overcome by using high grade distillate fuels for aero engines. However, despite the use of high grade fuel it was found that turbine components withdrawn from carrier-based aircraft and from helicopters exhibited severe high temperature corrosion which often resulted in the premature rejection of very expensive hardware. This type of damage, which is sometimes called sulphidation-corrosion, is primarily caused by reaction between sea salt residues carried by the combustion gas stream and the hot oxide-covered surfaces of aerofoil components. Hot corrosion has been the subject of ongoing research since the early 1950s and remains a somewhat controversial subject as evidenced by the considerable legacy of scientific and technological papers and excellent reviews that have been published 1-18.



FIG. 1—CORRODED MARINE PROTEUS TURBINE ROTOR BLADES

In consequence of the early deployment of gas turbines such as the marinized Proteus for fast patrol boats and hovercraft propulsion, and the AEI G6 engine for boost propulsion in 'combined steam and gas' systems, the Royal Navy quickly acquired experience of the damaging effects of hot corrosion. On a historical note, an example of severely corroded turbine blades withdrawn after approximately 1500 hours service in a marinized Proteus engine is shown in Fig. 1. Various countermeasures have been

developed and utilized in the wake of the initial experience, including filtration of the compressor intake air and fuel, compressor washing and inhibition, and the development of more corrosion-resistant blade and nozzle guide vane materials (viz. the superalloys) and improved coatings. In addition to these countermeasures, research work initiated at NGTE (now RAE) in the 1950 period has shown that certain fuel additives, based primarily on chromium compounds, can inhibit hot corrosion. Detailed information on these various developments can be found in the literature.

In this article an outline is presented of the developments in high temperature superalloys used for the manufacture of aerofoil components in aero and marine gas turbines. There is some commonality of these materials in industrial gas turbines. Advances in process technology for the manufacture of turbine blades are also described. Brief reference is made to the results of corrosion rig tests and engine experience of selected materials. Advances in protective coatings technology will be discussed in a subsequent article.



FIG. 2—CUT-AWAY VIEW OF AERO-ENGINE NOZZLE GUIDE VANE Courtesy of Rolls-Royce, Ltd.

NICKEL AND COBALT SUPERALLOYS

Early Alloy Developments

During the evolution of the gas turbine in the 1940s and throughout the 1950s and early 1960s high temperature materials research and development covered a broad range of metallic and non-metallic materials from high temperature steels, nickel and cobalt alloys to refractory metal alloys, cermets (ceramic + metallic mixtures) and ceramics. Despite the ingenuity, diligence, and enthusiasm demonstrated in these various materials R&D programmes, nickel and cobalt alloys have retained their prime status as 'bill of material' for the critical turbine rotor blades and nozzle guide vanes (NGVs), in today's engines. Their predominance has been sustained by materials developments coupled with advances in engineering design and process technology. Improved processing has made possible the manufacture of thin-walled aerofoil components containing a complex array of cooling channels typical of that required in high performance engines. FIG. 2 shows an example of the sophisticated cooling achieved for the high pressure nozzle guide vanes used in a modern aero engine.

Cobalt base superalloys were extensively used for turbine rotor blades and NGVs in some early designs of U.S. manufactured gas turbines. The cobalt alloy Stellite 31*, when processed by the vacuum melting route, has also been successfully used as the first stage turbine rotor blade material for the Proteus hovercraft engine. However, as they are not as strong as nickel superalloys used more generally for turbine rotor blading in recent years, cobalt superalloys have been restricted to use in more lowly stressed applications such as NGVs. Even, for the latter application cobalt superalloys have been partly replaced by nickel alloys. Compositions of superalloys discussed in this article are listed in TABLE I.

Alloy*	Ni	Cr	Co	Мо	W	Ta	Nb	Al	Ti	С	В	Zr	other
STELLITE 31	10.5	25.5	Bal	-	7.5	~	_	_	_	0.50	-	_	
MAR-M 509	10.0	23.5	Bal	7.0	3.5	-	-	-	0.2	0.60	-	0.50	
NIMONIC 75	Bal	20.0	- 1	-	- 1	-	-	_	0.4	0.08	-	_	
NIMONIC 80A	Bal	19.5	1.1	-	-	-	-	1.3	2.5	0.08	-	-	
NIMONIC 105	Bal	14.3	20.0	5.0	-	-	-	4.5	1.2	0.20	0.005	0.10	:
NIMONIC 108	Bal	14.8	20.0	5.0	-	-	-	4.7	1.2	0.15	0.008	0.15	
NIMONIC 115	Bal	15.0	15.0	3.5	-	-	-	5.0	4.0	0.15	-	_	
M 313	Bal	30.0	-	-	-	-	-	0.9	1.8	0.05	0.003	0.05	
IN 587	Bal	28.5	20.0	-	-	-	0.7	1.2	2.3	0.05	0.003	0.05	
IN 597	Bal	24.5	20.0	1.5	-	-	1.0	1.5	3.0	0.05	0.012	0.05	0.02 Mg
NIMOCAST 713C	Bal	12.5	_	4.2	-	-	2.0	6.1	0.8	0.12	0.012	0.10	Ũ
IN 100	Bal	10.0	15.0	3.0		-	-	5.5	4.5	0.18	0.014	0.06	1.0 Y
IN 738	Bal	16.0	8.5	1.7	2.6	1.7	0.9	3.4	3.4	0.17	0.010	0.10	
MAR-M 002	Bal	9.0	10.0	-	10.0	2.5	-	5.5	1.5	0.15	0.015	0.05	1.5 Hf
MAR-M 200	Bal	9.0	10.0	-	12.5	-	1.0	5.0	2.0	0.15	0.015	0.05	
IN 792	Bal	12.4	9.0	1.9	3.8	3.9	_	3.1	4.5	0.12	0.020	0.10	
IN 939	Bal	22.4	19.0	-	2.0	1.4	1.0	1.9	3.7	0.15	0.009	0.10	
IN 6201	Bal	20.0	20.5	0.55	2.4	1.4	1.0	2.4	3.5	0.03	0.800	0.06	
SX 60A	Bal	8.5	10.0		10.0	4.0	-	5.5	1.5	0.02	_	_	
CMSX 2	Bal	8.0	4.5	0.5	8.0	6.0		5.6	1.0	0.00006	0.003	0.01	
										max	max	max	
MMT 143	Bal	-	-	14.3	-	6.0	-	5.8	-	0.02	-	_	
RST 104	Bal	-	-	18.0	-	-	-	8.0	-	-	-	_	
RSR 185	Bal	-	-	14.3	6.2		-	6.8	-	0.02	-		
MA 754	Bal	20.0		-	-	-	-	0.3	0.5	0.05	-	-	$0.6 Y_2O_3$
MA 6000	Bal	15.0	-	2.0	4.0	2.0	-	4.5	2.5	0.05	0.010	0.15	$1.1 \ Y_2O_3$

TABLE I-Nominal chemical Composition of Nickel- and Cobalt-base Superalloys (weight %)

*All alloy names such as those prefixed IN, Inco, MA, MAR-M, Nimonic, Nimocast, Stellite, TD, Udimet, etc. are registered trade marks.

Numerous and more detailed accounts of the development of high strength superalloys are available in the metallurgical literature. Particularly noteworthy among the many excellent and comprehensive reviews tracing the technological development of superalloys are references 19 to 24. Clearly, materials developments for the critical turbine rotor blade application have been preferentially directed towards nickel superalloys. Historically the first nickel superalloy of engineering significance was Nimonic 75 alloy which consists essentially of a solid solution (mixture) of chromium in nickel; it also contains a small amount of carbon to form some metal carbide particles dispersed in the microstructure. Nimonic 75 alloy was developed in the U.K. at approximately the same time as a comparable alloy Inconel was developed in the U.S.A. These alloys possess a better combination of strength and oxidation resistance than stainless steels. The next significant step was the addition of aluminium and titanium to the simple nickel-chromium matrix to form a precipitate of the intermetallic compound Ni₃Al-Ti, gamma-prime, which produced a marked improvement in strength. Nimonic 80 alloy, introduced about 1941, is basically a 80% Ni-20% Cr alloy with the addition of 2.25% titanium and 1% aluminium; it has superior creep properties relative to Nimonic 75. This development satisfied the immediate engineering demand for a material with better creep strength at temperatures up to approximately 1100 K, combined with good oxidation and corrosion resistance, and the alloy was forgeable. A further series of wrought nickel alloys, trade marked as the Nimonic alloys, was developed in succession to satisfy the continuing engineering requirements for materials with yet better creep strength. These materials contained additions of refractory metals and increased levels of titanium that were needed to produce the required high temperature strength improvements. The Nimonic alloys when protected by simple aluminide coatings have given excellent service in successive generations of aero gas turbines burning distillate fuels. Alloys in this series such as Nimonic 105, 108, and 115 have also been employed for turbine blades in the Proteus, Tyne, and marine Olympus engines.

Later Developments in Superalloys

However, in an attempt to satisfy the service requirements of long life (several tens of thousands of hours) for industrial gas turbines operating in hostile (desert) environments and burning lower grade fuels, a further series of higher chromium content wrought nickel superalloys—M 313 (30% Cr), IN 587 (28.5% Cr) and IN 597 (24.5% Cr)—was developed. Creep-rupture data for selected wrought alloys²⁵ are shown in FIG. 3.

As the amount and type of alloying elements increased, vacuum melting was introduced into alloy manufacture because some of the alloy additions have a high affinity for oxygen and nitrogen which may be present in the atmosphere of the melting chamber. With the newer alloys, also, the limits of conventional forging technology were being approached at a time when the reliability of investment castings had improved to the extent where design engineers became more ready to accept precision-cast components. This stimulated further alloy development based on increasing additions of refractory and other alloying elements designed to maximize high temperature creep strength as the primary engineering requirement. The creep strength improvement, metallurgically speaking, is in consequence of refractory metal alloying elements strengthening the nickel matrix phase and also through increasing the volume fraction of the precipitation-hardening phase, gammaprime (Ni₃Al-Ti). The microstructure of a cast nickel superalloy (such as Nimocast 738 alloy which is the current material in several industrial and marine engines), as revealed by electron microscopy, is illustrated in FIG. 4.



Temperature (°C) for 100 hours rupture life at stress of 93N/mm²

FIG. 3—Stress-rupture temperature capability v. chromium content of blading alloys



FIG. 4-MICROSTRUCTURE OF NIMOCAST 738 ALLOY (×18 000)

This shows a high volume fraction of gamma-prime phase (as a cuboidal precipitate) that is uniformly dispersed in the nickel matrix.

Although considerable success was achieved in the development of alloys such as Nimocast 713C and IN 100 alloy, which have an enviable performance record in aero gas turbines, alloy design had become somewhat empirical. In order to achieve these improvements in creep strength the total aluminium plus titanium content was increased, whilst the chromium content was decreased in order to avoid the formation of topologically close-packed (tcp) phases such as sigma, or others such as the μ -phase of closely-related microstructure. These phases, based on transition element intermetallic compounds, are hard and brittle, often adopting a plate-like morphology in the microstructure (e.g. FIG. 5), and have been responsible for initiating premature failure of turbine blades and NGVs in service engines through loss of



FIG. 5-MICROSTRUCTURE SHOWING SIGMA PHASE IN NIMOCAST 713 ALLOY (×800)

creep strength and embrittlement. The microstructure shown in FIG. 5 was prepared from the fracture surface of a 2nd stage NGV segment withdrawn from a T56—A15 engine after 1900 hours service. It is noteworthy that the fracture path corresponds closely with the acicular sigma phase precipitate in the microstructure. The NGV was manufactured in Nimocast 713C alloy with a pack-aluminized coating for service. Fortunately a detailed scientific understanding of this problem has been developed and a procedure known as PHACOMP (an acronym for phase computation) is now routinely employed for predicting the propensity to such micro-structural instability in production heats of superalloys.

A further consequence of the need to reduce the chromium content of the high strength casting alloys is the attendant reduction in hot-corrosion resistance as with the wrought superalloys. During the 1960s and 1970s, in response to the acknowledged industrial requirements for cast superalloys with an improved balance between strength and corrosion resistance, International Nickel Co., Ltd., developed IN 738 alloy which matched the creep-rupture strength of the aero alloy IN 713C but with considerably improved

hot-corrosion resistance. Further attempts to increase strength whilst maintaining hot-corrosion resistance necessitated a reduction in chromium content and further modification of alloy composition with regard to titanium, tungsten, tantalum and niobium content. The resultant alloy, designated IN 792, possesses creep strength similar to that of the aero alloy IN 100 with corrosion resistance similar to that of IN 738²⁶. Data showing the creeprupture temperature capability versus hot-corrosion resistance (measured under laboratory conditions) for some well established nickel superalloys are reproduced in Fig. 6. It should be noted that considerable criticism has been



Fig. 6—Temperature capability for 10 000 hours rupture v. hot corrosion resistance of nickel superalloys



FIG. 7—TYNE RM1C TURBINE ROTOR BLADE AFTER 500 HOURS SALT CORROSION TEST

levelled at the use of various laboratory corrosion test procedures and although they can be used as a guideline for alloy development their ranking of the performance of the materials may not always be validated in reallife engine situations. For example, although most laboratory and high velocity corrosion rig test data indicate that IN 792 alloy is inferior to IN 738 alloy, a Tyne RM1C engine trial of approximately 2500 hours duration showed somewhat surprisingly that there was very little difference in performance between pack-aluminized blades made in IN 738 or IN 792^{27} .

FIG. 7 illustrates the condition of a turbine rotor blade withdrawn from a Tyne RM1C engine after only 500 hours trials testing under sea salt ingestion conditions at Pyestock. The trial, which was conducted several years ago, involved the combustion of standard F-76 Dieso with atomized sea water being ingested both into the fuel and the air intake. The blades were manufactured in Nimocast 738 alloy coated with a proprietary aluminide

coating and were most severely degraded on the pressure surface section adjacent to the internal cooling passages. Two modes of attack were observed, low and high temperature corrosion. The low temperature form of corrosion is characterized by the formation of a layered corrosion scale (FIG. 8) composed primarily of chromium oxide with residues identified as having a sea salt origin. This form of attack, which has also been observed elsewhere (even in the presence of expensive so-called overlay coatings) can be more



FIG. 8-LOW TEMPERATURE CORROSION ATTACK

catastrophic than that occurring at higher temperatures, and was found over heavily cooled regions of the aerofoil where the metal temperature was below 1020K. A sharp cut-off was observed between the regions of the aerofoil which had experienced the low temperature layered scale corrosion attack and the adjacent higher temperature sections of the aerofoil (i.e. above 1100K), which was characterized by sulphide penetration of the alloy ahead of the surface oxide film. Also, dependent on the severity of the attack, there was evidence of intergranular corrosion damage. Electron microprobe analysis data showing X-ray maps which indicate the chemical composition of the corroded section are in FIG. 9; the sulphidation front advancing into the substrate can clearly be identified.





X-ray sulphur

X-ray oxygen

Fig. 9—Electron probe micro-analysis data for high temperature (1100 K) corroded section of the blade in Fig. 7

Recent Developments in Superalloys

In consequence of the demand by European industrial turbine producers and users for a strong corrosion-resistant turbine blade material capable of operating for very long time between overhaul (TBO) at temperatures around 1123K, International Nickel developed IN 939 alloy, containing approximately 23% chromium²⁵. A very favourable review²⁸ has recently been published of the corrosion performance of IN 939 blades and vanes operating in industrial gas turbines for more than 30,000 hours. There are indications, however, that the alloy may not be as strong as IN 738LC alloy. Currently IN 939 is being trialled in various Rolls-Royce engines, including the Tyne RM1C. The trials are as yet incomplete but good corrosion results are anticipated in view of the overwhelming evidence derived from various high velocity corrosion rig tests^{25, 28, 29}.

Whilst considerable test and field experience has been gained with alloys such as IN 738, IN 792, etc., the search has continued for turbine blade materials with the strength level of IN 792 coupled with corrosion resistance at least equal to that of IN 738. One approach to this problem, used by Johnson Matthey, Ltd., has been to add platinum or other precious metals to nickel superalloys³⁰. A separate approach by Inco Alloyed Products Inc. (U.K.), working under contract from MOD(PE), has been to explore the potential of nickel alloys containing high concentrations of chromium and boron³¹. From this research an alloy, IN 6201, has been identified which from laboratory tests of mechanical properties and corrosion resistance satisfies the initial target requirements. Creep-rupture data³² measured on conventionally cast IN 6201 are shown in Fig. 10 in comparison with IN 738



Fig. 10—Creep-rupture data for conventionally cast IN 738, IN 792, and IN 6201 (thick section test pieces)

and IN 792. In addition to the laboratory corrosion tests, IN 6201 has also been evaluated in high velocity gas turbine simulator corrosion rig tests at ARE (Holton Heath) and Cranfield Institute of Technology. The results of these tests have been very encouraging; comparison data obtained for IN 6201, IN 738 and IN 939 at 973K using the ARE rig are shown in FIG. 11.



FIG. 11-RESULTS FROM HOT CORROSION TESTS AT 973 K IN THE ARE LP RIG

Corrosion data obtained for IN 6201 type alloy at higher temperatures have been published elsewhere²⁹. Although the corrosion rig test results obtained for IN 6201 appear attractive, some reservations have been expressed³³ concerning the likely performance of one alloy variant where high thermal shock may be encountered, e.g. in an engine situation. In the corrosion tests at 973K and 1023K, the IN 6201 variant initially corrodes at a faster rate than IN 939 and IN 738, though in the longer term the corrosion scale on IN 6201 type alloy thickens but remains adherent and the corrosion rate slows. In contrast, corrosion scales formed on both IN 738 and IN 939 spall and the loss of material for both alloys is greater at 600 and 1200 hours. Further work is in progress on IN 6201 including castability trials (conventional casting) for the manufacture of engine hardware, in addition to laboratory studies of the potential benefits of unidirectional solidification (UDS), etc.

ADVANCES IN MANUFACTURING TECHNOLOGY

UDS Casting Technology

The almost insatiable demand by design engineers for yet further increasing the turbine entry temperature (TET) taxed the ingenuity of materials scientists in developing stronger nickel and cobalt superalloys and also in devising the improved melting and casting procedures that were necessary for the manufacture of turbine blades and vanes. During the 1960 period in particular, rapid progress was made in exploring new alloy compositions and also in refining the ancient art of the lost wax shell moulding process for manufacturing superalloy aerofoil components containing increasingly sophisticated arrays of cooling channels. This period also coincided with a fairly intense period of activity in developing new process technology such as unidirectional solidification of superalloy components that was first deployed to advantage in military aero engines.



Fig. 12—Conventionally cast (left), directionally solidified polycrystalline (centre), and monocrystal (right) blades cast at Pyestock

More than twenty years have passed since VerSnyder and Guard³⁴ demonstrated that by modifying the conventional investment vacuum casting process it was possible to manufacture turbine blades with a controlled directional structure. They also demonstrated that the mechanical properties are significantly dependent on the grain orientation. Their technique was used initially to produce unidirectionally solidified (UDS) turbine blades in the alloy MAR-M 200 (see TABLE I) and in due course it was refined to produce blades consisting of one single grain (a monocrystal) of the alloy^{35, 36}. Similar work on solidification processing technology was also initiated at Pyestock³⁷⁻³⁹ during the same period and early examples of conventionally cast, UDS, and single crystal blades manufactured in this laboratory are shown in Fig. 12.

A schematic diagram of the Pyestock equipment used for controlled casting of aerofoil components and for metallurgical research purposes is shown in FIG. 13. The apparatus uses a 10 Kg capacity vacuum melting furnace which provides molten alloy feedstock to the controlled casting equipment which is housed in the same vacuum chamber. In operation, superalloy material is melted in a ceramic crucible using r.f. induction heating and the molten metal, at a controlled level of superheat, is poured into a shell mould which has a cooled metal chill at its base. The mould is surrounded by a resistanceheated furnace maintained at a temperature above the melting point of the solidifying alloy. After pouring into the hot mould, solidification of the



FIG. 13—RAE CASTING EQUIPMENT FOR MANUFACTURE OF UDS AND SINGLE-CRYSTAL BLADES

liquid starts at the bottom of the mould on the copper chill plate. Under the influence of the steep thermal gradient, grains grow vertically in a direction parallel to the flow, thereby forming the aligned structure. In order to maintain this aligned growth the mould is withdrawn from the furnace and finally through the mould lock to air for final cooling and removal of the components. Larger scale commercial UDS units in use today differ in some aspects of solidification procedure and invariably are automated, but they use the same principle of casting superheated metal against a chilled surface while concurrently establishing a suitable temperature gradient along the axial length of the mould.

The process has been commercially established for some years in the U.K. and elsewhere for the manufacture of blades and vanes of advanced design. The considerable performance benefits initially predicted from laboratory evaluation of UDS components have been confirmed in service engines.

UDS Alloys

The advantages gained by UDS of turbine blades and vanes are well known. For example, dependent on alloy composition, UDS has demonstrated at least a three- to four-fold improvement in thermal fatigue behaviour combined with some 20K to 30K temperature improvement in creep-rupture life; considerable improvements in tensile and creep ductility and microstructural soundness (decreased microporosity) are further benefits obtained from UDS. Experimental stress-rupture and thermal fatigue data obtained for selected aero type commercial nickel superalloys are shown in FIGS. 14 and 15 respectively. Comprehensive studies have also been done at RAE Pyestock, on the UDS of nickel and cobalt alloys designed for use in industrial and marine gas turbines, i.e. IN 738, IN 792, IN 939, IN 6201, and also Stellite 31 and MAR-M 509 (both cobalt base).

Mechanical property evaluation of UDS superalloys has also been done on thin section test pieces, consistent with section sizes (1 mm or less) used for the manufacture of heavily cooled turbine blades. A problem that is common to many conventionally-cast nickel superalloys is that when cast at section sizes below 1.5 mm they exhibit considerable reduction in strength properties and ductility; further, there is a tendency towards cracking and the overall yield of sound usable components is low. In contrast it has been generally found that, although UDS nickel superalloys exhibit some reduction in creep life compared with their thick section counterparts, their creep performance is at least comparable with the best thick section conventionally cast alloys. However, some of the stronger nickel superalloys such as IN 100 and IN 792 in UDS thin section form are prone to cracking along their longitudinal grain boundaries. This can be circumvented by modifying the alloy composition, e.g by the use of hafnium, etc., or alternatively by producing the castings as monocrystals. Lower strength alloys such as UDS IN 738LC and IN 939 do not appear to be susceptible to this problem. Recent trials at Pyestock have also shown that UDS thin section castings in IN 6201 are not prone to longitudinal cracking during routine processing and heat treatment. Some creep-rupture data for conventionally cast and UDS thin section IN 6201 alloy are shown in FIG. 16.

Single Crystal Casting Technology

Single crystal (SX) turbine blades can be grown by a similar procedure to that for UDS. The major difference in the casting technique is the use of a multiple turn constriction adjacent to the chill plate. During the early stages of solidification, even if two or more grains enter the helix, only one crystal survives which then grows through the aerofoil portion of the mould to produce the final component. Monocrystal components produced by this technique have a preferred growth orientation <001> structure. A large number of single crystal turbine blades and vanes has been cast using the above procedures and a production capability has been demonstrated.



FIG. 14—Stress-rupture lives of conventionally cast and UDS alloys



.

76



Fig. 16—Creep-rupture data for conventionally cast and UDS IN 6201 $(\frac{1}{4} \text{ MM} \text{ section})$

Single Crystal Alloys

Until recent years single crystal castings were of only marginal interest, primarily because demonstration hardware was manufactured from commercial superalloys that had originally been designed to give an optimal balance of properties when cast by conventional foundry techniques to produce an equiaxed grain structure. An essential requirement in such materials was the inclusion of small amounts of elements such as carbon, boron and zirconium that are collectively used for strengthening the grain boundary region. However, when such materials are employed for monocrystal components, although they exhibit some improvement in creep-rupture properties in the transverse growth direction due to the absence of weak grain boundaries, they offer little improvement relative to the polycrystalline UDS alloys. The realization that, with the exception of a small amount of carbon, other grain boundary alloying elements (boron and zirconium) are superfluous to monocrystal superalloys has permitted a new approach to alloy design in that the composition can be tailored to make stronger and more refractory materials. The development of new alloy compositions coupled with refinement of casting procedures utilizing seed crystals to give control of both the longitudinal and transverse orientation of the component has been used advantageously in the U.K. and elsewhere for R & D and pre-production purposes. A diagram of a seeded single crystal mould used at Pyestock and wax models of castings are shown in FIGS. 17 and 18.



FIG. 18—WAX MODELS OF SINGLE CRYSTAL CASTINGS

Stress-rupture and creep-rupture data for an experimental single crystal alloy (SX 60A) developed at Pyestock for aero gas turbines are shown in FIGS. 19 and 20. Comparison is made with advanced UDS materials and ODS*/mechanically alloyed materials (discussed later). SX 60A compares favourably with the best chromium-containing monocrystal superalloys developed worldwide. In general the chromium-containing monocrystal superalloys offer a creep-rupture strength advantage of some 20K to 30K over a range of temperature, relative to their UDS counterparts. Some interest has been shown in U.S.-developed chromium-free monocrystal superalloys based on compositions such as Ni-13Al-9Mo-2Ta or Ni-15 · 4Al-8 · 7Mo-2W (atomic %) which contain large amounts of refractory metal elements for providing creep strength. Further high temperature advances can be obtained through stress coarsening, or 'rafting', of the structure.⁴¹ These materials offer considerable high temperature creep strength advance over the chromium-containing monocrystal alloys such as SX 60A, the Rolls-Royce developed SRR 99, and *oxide dispersion strengthened

J.N.E., Vol. 29, No. 1



Fig. 19—100-hour stress-rupture v. temperature for UDS and single crystal alloys (density corrected)



Fig. 20—100-hour creep-rupture v. temperature for UDS, ODS, and single crystal alloys (density corrected)

some of the Cannon Muskegan commercial CSMX range of alloys,⁴² but are considerably inferior in oxidation and hot-corrosion resistance. Despite this limitation there still exists a reasonable possibility of using chromium-free single crystal components in short-life, high performance, military engines when protected by advanced overlay coatings.

Whilst the aero gas turbine has provided the major impetus to-date for the development of monocrystal turbine blade alloys, effort has also been directed in both the U.S.A. and U.K. to find suitable compositions of single crystal alloys with an optimal balance of creep strength and improved hotcorrosion resistance for use in marine power plants. The U.S. Navy programme with Pratt & Whitney Aircraft (PWA) is directed towards nickel base blade alloys containing chromium additions from 12% to 27% with selected additions of titanium, aluminium, etc., to give the required balance of structural and mechanical properties. Monocrystal alloy work at RAE has been primarily concerned with optimizing the composition of variants of IN 792 alloy particularly with regard to the effects of the minor alloying additions, boron, carbon, and zirconium. It has been shown that the retention of small amounts of boron and carbon (0.02 and 0.03%) in IN 792 alloy enhances the creep-rupture properties. Further possibilities for monocrystal turbine blades may centre around the development of variants of IN 6201 type alloys.

POWDER TECHNOLOGY

Early Developments

Although significant progress has been made in superalloy blade and vane materials utilizing conventional ingot melting and mechanical working, and through advances in precision casting technology, these advances have been challenged by continuing developments in powder metallurgy. The main incentives for using consolidated superalloy components made by powder processing are derived from the better control of homogeneity of microstructure and grain size that should result in a superior overall balance of mechanical properties (creep, fatigue, and toughness) with improved workability. Prior expertise was demonstrated in the development of a powder processed turbine blade material when, during the mid 1960s, GEC engineers working under contract to the Ministry of Aviation (through NGTE) established a manufacturing route (isostatic pressing and sintering) for turbine rotor blades based on a powder variant of Nimonic 115 alloy. The work progressed to the stage where Rolls-Royce machined more than a hundred blades from pressed and sintered blanks and successfully tested them in a development engine. Whilst the demonstration highlighted the potential of powder processed superalloy blade materials, work ceased soon afterwards when the early fears over the possible risk of using conventionally cast superalloy blades were dispelled following their successful deployment in a large range of gas turbines.⁴⁴

Oxide Dispersion Strengthening (ODS)

In recent years there has been a resurgence of interest in the possibility of manufacturing superalloy components with yet higher temperature capability than monocrystal blade designs, using powder processed stock. One approach, which originated some twenty or so years ago, employs a finely dispersed inert, non-metallic (usually a refractory) oxide phase into a superalloy matrix in order to provide improved microstructural stability and strength retention at temperatures where the Ni₃Al type precipitate responsible

for strengthening conventional superalloys (including single crystals) is becoming unstable. The alternative strategy involves manufacturing components with a highly sophisticated cooling configuration—wafer blades⁴⁵—in novel alloy compositions produced by rapid solidification rate powder technology.

Mechanical Alloying (MA)

Although a number of simple oxide dispersion strengthened (ODS) alloys such as TD Ni (nickel with 2% ThO₂) and TD Ni Cr (Ni-20Cr-2ThO₂) were produced commercially in the 1960s, their strength, particularly at intermediate temperatures, was too low for them to be used for turbine blades. Efforts were subsequently made to produce stronger materials combining both precipitation hardening and oxide dispersion strengthening but it was not until the early 1970 period that a suitable manufacturing route⁴⁶, known as Mechanical Alloying, was developed. This is essentially a dry, high energy ball-milling process in which a blended mixture of elemental and master alloy powders together with a fine dispersion ($<0.1 \ \mu m$ in size) of yttrium oxide is processed under controlled conditions at or near room temperature. Homogeneous mixing of the charge occurs because of the cold welding together of smaller particles and the fracturing of larger composite particles. These processes successively sub-divide and refine the internal structure of the particulates ensuring a uniform distribution of yttrium throughout the material. The dispersion strengthened powders can be consolidated and further fabricated by standard methods used for manufacturing bar, sheet, etc. However, in order to achieve the high temperature creep strength required for aerofoil components precise control of the overall thermomechanical working sequence is necessary in order to produce directional recrystallization during the subsequent zone annealing operation. Since the process can be carried out on nickel alloys containing elements such as titanium and aluminium, the usual age-hardening treatments are applied to the superalloy base, and the final material exhibits precipitation strengthening at intermediate temperatures combined with dispersion strengthening at high temperatures.

The structure of directionally recrystallized bar stock in MA 6000 alloy is illustrated in FIG. 21. The specific creep rupture strength of the strongest mechanically alloyed blade material MA 6000 over a range of temperature is compared in FIG. 20 with those of other advanced blade alloys made by directional solidification and monocrystal technologies respectively. This shows that MA 6000 is stronger than the best single crystal alloys at temperatures above about 1223K whereas the UDS and single crystal alloys are stronger below this temperature. Because of the strength deficiency of MA 6000 at lower temperatures and the facility to produce cast single crystal blades with sophisticated cooling configurations to cope with high temperatures it appears that the dispersion hardened materials may only find limited applications as blade materials in highly rated small engines where, because of geometric constraints, solid blades may be preferred to cooled aerofoils.

Although ODS alloys produced to date have not satisfied the mechanical property requirements for turbine rotor blades, because of their excellent blend of tensile, creep and thermal fatigue properties at elevated temperatures they offer considerable potential for nozzle guide vanes. General Electric Co. in the U.S.A. were quick to recognize the potential of utilizing the ODS alloy MA 754 (Ni-21Cr-0.6% Y₂0₃) as a high pressure nozzle guide vane material in the F404–400 aero engine.⁴⁷ It has also been shown that MA 754 alloy in the form of flat bar possesses exceptional thermal fatigue resistance which is derived from its <100> texture induced by thermomechanical



FIG. 21—MICROSTRUCTURE OF MA 6000 ALLOY (a) is a low magnification view, (b) a replica electron micrograph showing detail of the age-hardening precipitate (Ni₃Al), and (c) a higher magnification view showing the very fine yttria particles both within the matrix phase and in the gamma-prime particles. A coarser secondary dispersion of carbonitride particles is also present.

working. The good corrosion resistance of MA 754 alloy has been demonstrated in rig tests at 1123K and 1223K⁴⁸, and also by a simulated sea salt ingestion test on a F404 engine. On completion of this test, which was designed by the U.S. Navy to represent over 1000 hours of engine operation in aircraft carrier based service, the MA 754 alloy nozzle guide vanes showed no perceptible corrosion.

Rapid Solidification Rate Technology

Considerable interest is also being shown in rapid-solidification-rate technology (RST) by which particulate, thin surface films or ribbon materials are produced by utilizing very fast cooling rates (>1000K/sec) from the pre-alloyed liquid state, followed by subsequent consolidation by standard metallurgical techniques into bulk pieces or components. Various methods for producing RST materials by atomization, melt spinning, and laser processing are illustrated schematically in Fig. 22. Pioneering work on RST is credited to Pol Duwez⁴⁹, who in 1960 studied splat quenching from the molten state. His work opened up the possibility of producing materials with new microstructure/property relationships because of the prospect of enhancing the solubility of alloying additions to metal matrices under very high rates of cooling (>1000K/sec). However it was not until the mid-1970 period, with the emergence of the PWA centrifugal atomizing process (shown schematically in Fig. 22a) for producing rapidly solidified superalloys on a



- FIG. 22—RAPID SOLIDIFICATION PROCESSING TECHNIQUES
 - (a) CENTRIFUGAL ATOMIZATION
 - (b) WATER COOLED COPPER CHILL
 - (c) SELF-QUENCHING

sufficient scale and with suitable quality, that industrial interest was excited. In the PWA process for making RST powder⁵⁰, a vacuum induction melted alloy stream is poured under controlled conditions on to a horizontal disc spinning at approximately 25,000 r.p.m. Molten alloy is centrifuged into droplets ranging from $10\mu m$ to $100 \mu m$ which are instantly frozen by sonic jets of helium. The cooling rate achieved by helium quenching is in the range of 10⁶K/sec, which offers the possibility of producing novel alloys with unique (microhomogeneous) microstructures. Alloy powders produced by this process are claimed to have a higher incipient melting point (up to 82K higher in certain instances), which should also permit higher solution temperatures of the consolidated stock with resultant increases in strength. In order to develop optimal strength properties following compaction of the RST powders by extrusion, directional recrystallization can be employed to produce elongated structures analogous to those obtained by the same process in ODS alloys. Such behaviour is not confined to RST powders as it has been previously observed in extruded rod produced from conventionally atomized superalloys.

RST Material Properties and Potential Applications

Currently, mechanical property data obtained on selected chromium-free nickel superalloys show significant high temperature creep strength advantage relative to the best commercially available monocrystal compositions that contain chromium additions and also to the most advanced superalloys produced by mechanical alloying. However, similar creep strength benefits may also be obtained, with more advantageous control of component orientation (or texture) and more cheaply, if the alloy produced by the RST route is itself produced by the single crystal casting process. It is noteworthy that the strongest RST alloys identified to date are based on compositions containing large amounts of refractory metals and very little chromium; hence their oxidation and corrosion resistance is suspect. Nevertheless, it has been already demonstrated that RST superalloys may offer potential for a very remarkable pay-off in advanced gas turbines by being a suitable material for the manufacture of wafer blades. Fabrication studies with RST nickel superalloy materials (of the Ni Mo Al type) have shown that these materials can be processed in a similar manner to that used for the manufacture of standard powder-processed components. One material (6.8 Al-14.5 Mo-6.2 W-0.06%C) has demonstrated superplastic behaviour under appropriate isothermal forging and hot rolling conditions which makes it readily formable into strip stock from which wafers can be manufactured. The wafers are then photo-etched to the desired cooling configuration before being assembled and vacuum diffusion bonded together. Thereafter, the component is subjected to a directional recrystallization heat treatment in order to produce the columnar microstructure required for higher temperature creep strength before final machining^{40, 45} by Electro Discharge Machining (EDM) or Electro Chemical Machining (ECM), and inspection. The final operation is that of applying a protective coating.

The wafer blade design utilizing the improved temperature capability of RSR 185 alloy is claimed to offer a potential TET increase of 600°F (333K) or more, for equivalent operating life, over the existing 'state-of-the-art aerofoil'51, or alternatively an approximate 50% increase in thrust-to-weight ratio over the current directionally solidified nickel superalloy MAR-M 200 + Hf.⁴⁰ Whilst the wafer blade provides an impressive demonstration of advanced manufacturing technology for aero gas turbine engine components it is unclear whether it can provide cost and performance benefits for long term service conditions even under conditions where high quality distillate fuels are used and the operating environment (dust and other contaminants) is comparatively clean. The potential spin-off of the wafer blade for marine propulsion engine components is difficult to assess at this time, in view of the distinctly more hostile corrosive and sometime erosive environments in which the components are required to operate. However, the prospect will become much clearer when the results are published of the programme sponsored by ERDA (Energy Research and Development Authority) to assess wafer cooling technology (of both vanes and blades) in an industrial gas turbine.

CONCLUDING REMARKS

Considerable advances have taken place in the development of high strength superalloys used in the manufacture of critical high temperature aerofoil components in gas turbines. Despite the considerable R&D effort applied to alternative metallic and non-metallic materials, nickel and cobalt alloys have retained their prime status as 'bill of material' for critical turbine rotor blades and nozzle guide vanes in advanced gas turbines. This status has been sustained through alloy developments coupled with advances in the way that the materials are produced through various melting, casting and subsequent processing routes, coupled with advances in engineering design. For nickel superalloys the process technology has changed from conventional wrought products, through vacuum melting and casting, to producing components by conventional casting, unidirectional solidification, or as single crystals. Useful advances have also been made in the manufacture of components by the powder processing routes stemming from the early GEC development of sintered turbine blades to the extremely sophisticated wafer blade which is currently being manufactured from high purity, rapidly solidified powder stock and processed by the most advanced processing route available to date.

The driving force behind these developments has been the aero gas turbine engine. In view of the commonality of materials technology, advantage has been taken, where appropriate, to utilize these advances for industrial and marine gas turbine power plant. For aero-engines operating with high grade distillate fuel the life-limiting component is usually the high pressure rotor blade which ideally should not fail by corrosion processes until the creep or fatigue life is exhausted. For marine gas turbines in the early days hot corrosion was clearly the life-limiting factor. Considerable progress has been made in minimizing hot corrosion by exercising good fuel husbandry, by the use of air filtration, etc., and through general improvements in the materials used for manufacture.

Whereas some twenty years ago marine power plant life was seldom more than one or two thousand hours, today's engines are expected to survive many thousands of hours before overhaul. In the longer term the current trend in superalloy design and process technology, coupled with the use of advanced protective coatings, should result in yet further improvement in engine performance, reliability and life.

References

- 1. Sykes, C. and Shirley, H.T.: Scaling of heat resistant steels; Symposium for High Temperature Steels and Alloys for Gas Turbines, London Iron and Steel Institute Special Report, 43, 1951, pp. 153-169.
- 2. Simons, E. L. and Browning, G. V.: Sodium sulphate in gas turbines; Corrosion, 11, 12, 1955, pp. 17-25.
- 3. Hancock, P.: The Corrosion of nickel chromium alloys in sulphur-containing atmospheres at high temperatures; *Proc. 1st International Conference on Corrosion*, Butterworth, London, 1961, pp. 193-201.
- 4. Lewis, H. and Smith, R. A.: Corrosion of high temperature nickel base alloys by sulphate chloride mixtures; *Proc. 1st International Conference on Corrosion*, Butterworth, London, 1961, p. 202.
- 5. Dean, A. V.: Investigation into the resistance of various nickel and cobalt base alloys to sea salt corrosion at elevated temperatures: N.G. T.E. Report 267, 1965.
- 6. Seybolt, A. U.: Sulphur diffusion through Cr_2O_3 at 1000°C; Trans. Met. Soc. A.I.M.E., 242, 1968, pp. 752–754.
- 7. Hancock, P.: Corrosion of alloys at high temperatures in atmosphere consisting of fuel combustion products and associated impurities—a critical review; H.M.S.O., London, 1968.
- 8. Bornstein, N. S. and De Crescente, M. A.: The Role of sodium in the accelerated oxidation phenomenon termed sulfidation; *Trans. Met. Soc. A.I.M.E.*, 2, 1971, p. 2875.
- 9. Goebel, J. A. and Petitt, F. S.: Na₂SO₄-induced accelerated oxidation (hot corrosion) of nickel; *Met. Trans.*, 1, 1970, pp. 1943-1954.
- 10. Stringer, J.: Hot corrosion in gas turbines; Metals and Ceramics Information Center Report, MCIC 72-08, 1972.
- 11. Hart, A. B. and Cutler, A. J. B., eds.: C.E.G.B. Conference on Deposition and Corrosion in Gas Turbines; Applied Science Publishers, 1973.

- 12. Condé, J. F. G.: What are the separate and interacting roles of sulphur, sodium and chloride in hot corrosion?; Specialist Conference on High Temperature Corrosion of Aerospace Alloys, Lyngby, Denmark, AGARD-CP-120, 1972.
- 13. Restall, J. E.: The Effects of salt and carbon particles on the erosion and corrosion behaviour of gas turbine materials; N.G.T.E. Report R339, 1975.
- 14. Proc. 2nd U.S./U.K. Conference on Gas Turbine Materials in the Marine Environment, Castine, Maine, 1974.
- 15. Proc. 3rd U.S./U.K. Conference on Gas Turbine Materials in the Marine Environment, Bath, U.K., 1976.
- 16. Proc. 4th U.S./U.K. Conference on Gas Turbine Materials in the Marine Environment, Annapolis, 1979.
- 17. Condé, J. F. G.: The Control of hot corrosion in marine gas turbines; *Journal of Naval Science*, 19, 1981, pp. 124–133 and 184–190.
- 18. Proc. COST 50 Conference on High Temperature Alloys for Gas Turbines, Reidel Publishing Co, 1982.
- 19. Betteridge, W.: The Nimonic Alloys; E. Arnold, London, 1959.
- 20. Betteridge, W. and Heslop, J.: The Nimonic Alloys; E. Arnold, London, 1974.
- 21. Sims, C. T. and Hagel, W. G.: The Superalloys; J. Wiley, 1972.
- 22. Sullivan, C. P., Donachie, M. J. and Morral, F. R.: Cobalt-base superalloys; Cobalt Information Centre, 1970 (Monograph Series).
- 23. International Symposium on Structural Stability in Superalloys, American Society of Metals, 1968.
- 24. Meetham, G. W., ed.: The Development of Gas Turbine Materials; Applied Science Publishers, 1981.
- 25. Shaw, S. W. K.: The Development of IN 939; Proc. 3rd U.S./U.K. Conference on Gas Turbine Materials in the Marine Environment, Bath, U.K., 1976.
- 26. Shultz, J. W. and Hulsizer, W. R.: Laboratory development of corrosion resistant nickelbase superalloys for gas turbines: Proc. 2nd U.S./U.K. Conference on Gas Turbine Materials in the Marine Environment, Castine, Maine, 1974.
- 27. Davis, F. N. and Grinnell, C. E.: Engine experience of turbine rotor blade materials and coatings; A.S.M.E. Gas Turbine Conference, Wembley, 1982, Paper no. 82-GT-244.
- Gibbons, T. B. and Stickler, R.: IN 939-metallurgy, properties and performance; Proc. COST 50 Conference on High Temperature Alloys for Gas Turbines, Reidel Publishing Co., 1982, pp. 369-393.
- 29. Condé, J. F. G., Booth, G. C. Taylor, A. F. and McCreath, C. G.: Hot corrosion in marine gas turbines; *Proc. COST 50 Conference on High Temperature Alloys for Gas Turbines*, Reidel Publishing Co., 1982, pp. 237-247.
- 30. Coupland, D. R., McGill, C. R., Corti, C. W. and Selman, G. L.: Platinum-enriched superalloys for enhanced corrosion resistance at elevated temperatures; *Institution of Metallurgists Conference on Environmental Degradation of High Temperature Materials*, 1980.
- 31. Shaw, S. W. K.: Nickel-base superalloys; British Patent Spec. 1544720, 1979.
- 32. Shaw, S. W. K.: private communication, 1982.
- 33. Taylor, A. F.: private communication, 1984.
- 34. Versnyder, F. L. and Guard, R. W.: Directional grain structures for high temperature strength; Trans. American Society of Metals, 52, 1960, pp. 485-493.
- 35. Piearcey, B. J. and Versnyder, F. L.: Single crystal alloy extends turbine blade life; SAE Journal, 74, 1966, pp. 36-43.
- 36. Versnyder, F. L. and Shank, M. R.: The Development of columnar grain and single crystal high temperature materials through directional solidification; *Materials Science & Engineering*, 6, 1970, pp. 213-247.
- 37. Northwood, J. E. and Homewood, T.: Experiments on the unidirectional solidification of the nickel base alloy 713C; Proc. 9th Commonwealth Mining and Metallurgical Congress, 1969.
- 38. Northwood, J. E. and Homewood, T.: Unidirectional solidification of high temperature materials for gas turbines; *Metallurgia and Metal Forming*, 41, (9), 1974, p. 254.
- 39. Glenny, R. J. E., Northwood, J. E. and Burwood-Smith, A.: Materials for gas turbines; International Metallurgical Review (193), The Metals Society, 1975.
- 40. Versnyder, F. L.: Superalloy technology-today and tomorrow; *High Temperature Alloys for Gas Turbines*, ed. by R. Brunetaud et al.; Reidel Publishing Co., 1982.
- 41. Pearson, D. D., Lemkey, F. D. and Kear, B. H.: Stress coarsening of γ' and its influence on creep properties of a single crystal superalloy; *Superalloys* 1980, A.S.T.M.

- 42. Drapier, J. M.: Precision casting of turbine blades and vanes; *High Temperature Alloys for Gas Turbines*, ed. by R. Brunetaud et al.; Reidel Publishing Co., 1982.
- 43. Strachan, J. F., Grimwade, M. F. and Coomber, H. J.: Sintered turbine blades; GEC Journal, 34, (2), 1967, pp. 46-53.
- 44. Weaver, M. J.: Powder metallurgy and the aero gas turbine engine; *Powder Metallurgy Group Meeting (Edinburgh), The Metals Society*, Oct. 1983.
- 45. Sellars, R., Dahlberg, D. E. and Calvert, G. S.: New approaches to turbine aerofoil cooling and manufacturing; AIAA/SAE 13th Propulsion Conference, Orlando, Florida, 1977.
- 46. Benjamin, J. S.: Dispersion-strengthened superalloys by mechanical alloying; *Met. Trans.*, 1, 1970, pp. 2943-2951.
- 47. Crawford, W.: Oxide dispersion-strengthened materials in advanced gas turbine engines-MA 754 vanes; Inco MAP Conference on Frontier of High Temperature Materials, 11, London, 1983.
- 48. Huber, P.: Hot corrosion testing of oxide dispersion-strengthened nickel base alloys; Inco MAP Conference on Frontiers of High Temperature Materials, 11, London, 1983.
- 49. Duwez, P., Willens, R. H., and Klement, W.: Continuous series on metastable solid solutions in silver-copper alloys; J. Applied Physics, 31, 1960, p. 1136ff.: and Rapid quenching of liquid alloys; Trans. Met. Soc. A.I.M.E., 227, 1963, p. 365ff.
- 50. Anon.: Metal Powder Report, 36, (9), 1981, pp. 425-432.
- 51. Anderson, R. E., Cox, A. R., Tillman, T. D. and Van Reuth, E. D.: Use of RSR alloys for high performance turbine aerofoils; *Proc. 2nd International Conference on Rapid Solidification Processing, Reston, Virginia, Claiters Publishing Division, 1980.*