

NICKEL, COBALT AND TITANIUM-BASED ALLOYS – FROM AIRCRAFT VEHICLES TO MEDICAL APPLICATIONS – REVIEW

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Abstract

Since the introduction of nickel, cobalt and titanium-based alloys in the early 1950s, these materials in a relatively short time became backbone materials for the aerospace, energy, chemical industry and even medicine. The combination of excellent mechanical properties, corrosion resistance and bio-compatibility renders these alloys the best material choice for many critical applications. This review describes the results realized through the research in the Department of Materials Science in “Vinča” Institute. The emphasize was given to the relation between the microstructure and mechanical properties of conventionally cast nickel and cobalt-based superalloys, as well as directionally solidified and single crystal castings of nickel-based superalloys. The special attention was paid to the development of vacuum melting and casting technology for processing surgical implants made of a titanium-based alloy.

Key words: high-temperature alloys, titanium alloys, melting and casting technology, microstructure, strength, medical application.

Introduction

Evolution of aircraft has required continual improvements in materials properties because increased speed raises the heating of the skin from friction with the air and increased power raises the temperature of the engine. Skin materials have progressed from wood and fabric to advanced alloys of aluminum, titanium and composite materials based on graphite fibers in polymer and graphite matrix. In engines nickel and cobalt alloys have replaced steel.

Many of advanced metals currently in use were developed with a single application in mind: the aircraft gas-turbine, or turbojet, engine. The components in a gas-turbine engine are exposed to extreme conditions of every kind: high temperatures, corrosive gases, vibrations and high mechanical loads due to centrifugal forces. An

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engine is started, accelerated, decelerated and stopped every time the airplane propels, takes off and lands. The repetition of this cycle can lead to a kind of failure known as low-cycle fatigue, in much the same way that bending a wire back and forth repeatedly can cause it to break because of “metal fatigue”.

The basic design of the turbojet engines remained essentially the same for nearly 30 years. As metallic materials have been produced to withstand higher temperatures and greater stresses, they have been incorporated directly into engines, replacing components of less suitable materials and thereby increasing performance and reliability. The construction of turbojet engines has been one of the main driving forces in the development of advanced metals and the gas-turbine engine presents almost every kind of severe condition likely to be encountered by an advanced metal in the context of the modern aircraft gas-turbine engine.

A typical turbojet engine consists of three main sections called the compressor, the combustion chamber and the turbine (Fig. 1).

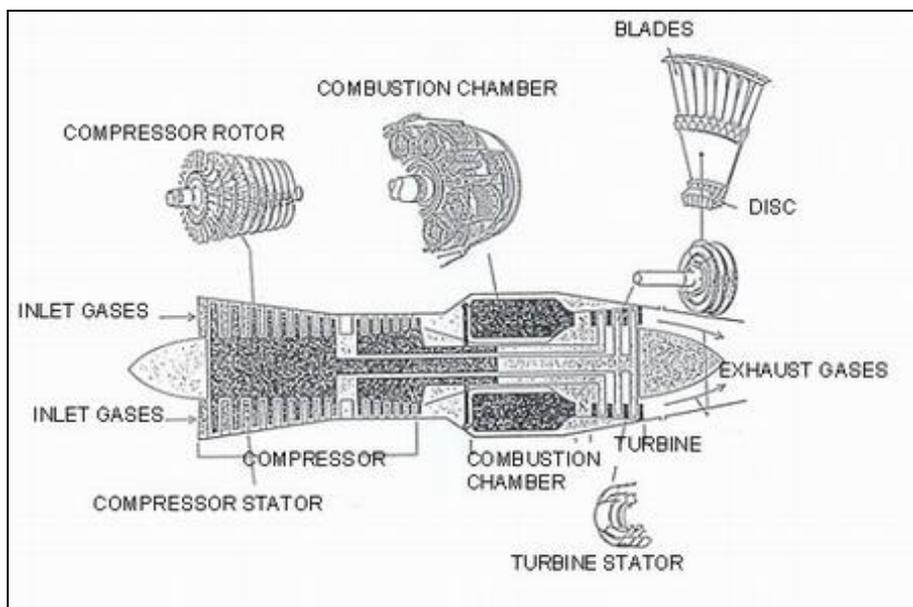


Fig. 1. Aircraft turbojet engine.

The components in the various sections of the engine have different structural requirements. The blades and vanes in the compressor must be able to withstand aerodynamic loads, and the rotating blades must also resist creep, i.e. the tendency to elongate gradually because of the centrifugal force. The disks that carry rotating blades must have a high load-bearing capacity in order to hold the blades against centrifugal forces. Turbine blades must also be able to withstand corrosive gases and far higher temperatures than are encountered in the compressor. Components throughout the engine must have very stable microstructures in order to maintain their properties over long periods of exploitation.

The iron, cobalt, or nickel-based alloys being used for these applications are called superalloys and are generally used at temperatures above 800 °C, i.e. often in

excess of 0.7 of the melting temperature. Iron, cobalt and nickel are transition metals with consecutive positions in the Periodic table of elements. The nickel-based superalloys are most widely used. Their applicability is based on the presence of Cr, especially to impart oxidation resistance, and other alloying elements to increase high-temperature strength, especially creep resistance.

Although cobalt, nickel, and titanium-based alloys are applied in both as-cast and wrought forms, this paper will be focused to alloys processed by melting and casting technology since complicated forms of many products may be produced by melting and casting technology.

2. NICKEL-BASED SUPERALLOYS

Phases and structure. Nickel-based superalloys consist of the austenitic face-centered-cubic (f.c.c.) matrix phase γ together with a variety of secondary phases. The principal secondary phases are carbides MC , $M_{23}C_6$ and M_6C and γ' f.c.c. ordered $Ni_3(Al,Ti)$ intermetallic compound. Strength of Ni-based superalloys derives from the difficulty with which single dislocations move through cuboids of γ' phase (Fig. 2).

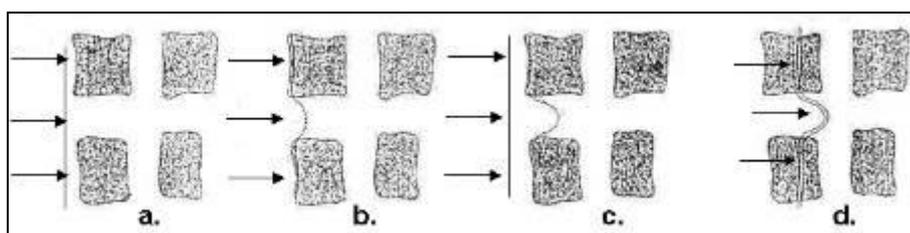


Fig. 2. Dislocations and the γ' phase particles [1].

A dislocation moves relatively easily through the undeformed γ matrix of the superalloy (a). Because the γ' phase is ordered, however, a single dislocation cannot move through it easily and so the cuboids of γ' in the matrix pin moving dislocations in place (b), making the metal more difficult to deform. When a second moving dislocation (c) joins the first one, the dislocation pair can move together through the γ' cuboids with a small high-energy antiphase boundary between them (d). The superalloy, therefore, resists deformation and is harder than a conventional alloy.

Carbides may provide limited strengthening directly (e.g. through dispersion hardening) or, more commonly, indirectly (e.g. through stabilizing grain boundaries against excessive shear). In addition to those elements that produce solid solution hardening and promote carbide and γ formation, other elements (e.g. B, Zr, Hf, Ce) are added to enhance mechanical and chemical properties. Table 1 gives a generalized list of ranges of alloying elements and their effects on superalloys on superalloys properties.

Table 1. Common ranges of main alloying additions and their effects on superalloys

Element	Range, wt. %	Effect
Cr	5-25	Oxidation and hot corrosion resistance; carbides; solution hardening
Mo, W	0-12	Carbides; solution hardening
Al	0-6	Precipitation hardening; oxidation resistance; γ' former
Ti	0-6	Precipitation hardening; carbides; γ' former
Co	0-20	Affects amount of precipitate
Ni	Balance	Stabilizes γ phase; forms hardening precipitates
Nb	0-5	Carbides; solution hardening; precipitation hardening
Ta	0-12	Carbides; solution hardening; oxidation resistance; γ' former

Table 2. Chemical Composition of Some Typical Superalloys for Casting Application

Alloy	Alloying elements, wt. %									
	Co	Cr	Ti	Al	Mo	C	Zr	B	Other	Ni
IN-713LC		-	0.6	5.9	4.5	0.05	0.1	0.01	2Nb	Bal.
IN-100	10	15	4.7	5.5	3	0.18	0.05	0.14	1V	Bal.
B 1900	9	10	1	-	6	0.1	0.1	0.15	4Ta	Bal.
Mar-M200	9	10	2	5	-	0.15	0.05	0.15	12W; 1Nb	Bal.

Conventional melting and casting practice. To make a conventional turbine blade, molten metal is poured into a ceramic mold (which is preheated to about half the temperature of the melt) and allowed to solidify. The final result is a fine-grained polycrystalline structure in which the individual grains are oriented randomly. A number of superalloys, particularly those with cobalt and iron, are air melted by various methods applicable to stainless steels. However, for most nickel-based superalloys vacuum induction melting (VIM) is required as the primary melting process. The use of VIM reduces interstitial gases (oxygen and nitrogen) to low levels, enables higher and more controllable levels of Al and Ti (along with other relatively reactive elements) to be achieved and results in less contamination from slag or dross formation than air melting.

Nickel and cobalt-based superalloys with high volume fraction (V_f) of γ' phase are processed to complex final shapes by investment casting. The process of investment casting (Fig. 3) starts with the production of expendable pattern, usually of wax, from pattern die. The use of an expendable pattern has been regarded as a distinguishing feature of the investment casting process. Patterns are mounted onto a wax runner system to form an assembly which is covered or invested with a fine coating of refractory (mostly Al_2O_3 or ZrO_2) powders; it is this process of investment that gives the process its name.

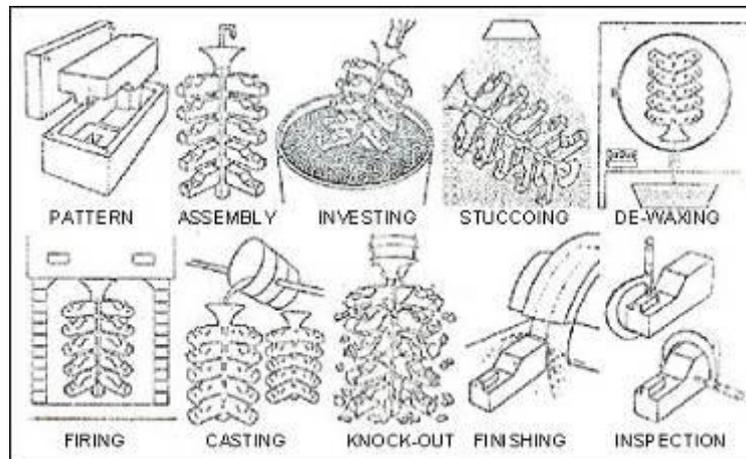


Fig. 3. Diagrammatic representation of investment casting process (ceramic shell mold) [2].

In the massive production ceramic shell technique, the pattern is invested with successive layers of refractory powder until a complete shell has been formed. The mold is de-waxed and fired to induce strength; molten metal is poured into the hot mold and, after cooling of the metal, the mold is broken to leave castings which are then removed from the runner system and finished according to customer requirements. The process converts the molten metal in a single operation to precision engineered components, with minimum wastage of (often expensive) material and minimum machining requirement. It is, indeed, the archetype of near-net-shape forming.

Microstructural characterization. Primary carbides, mainly MC, are first formed during cooling of the superalloy melt. With further cooling of the melt the γ phase first solidifies and with further decrease of temperature small cuboids of the γ' phase is precipitated in the γ matrix. At the end of solidification, the remaining melt solidifies as the mixture of two phases, i.e. $\gamma + \gamma'$ eutectic. The microstructure of as-cast IN-100 superalloy is shown in Fig. 4.

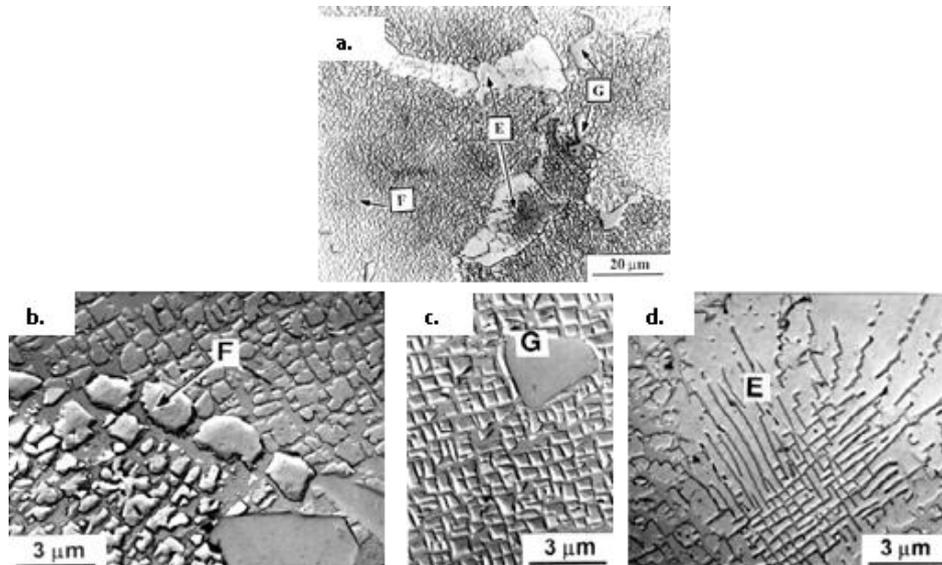


Fig. 4. Microstructure of as-cast IN-100 superalloy. E- $\gamma + \gamma'$ eutectic; F- γ' particles; G-MC carbides. a. Optical microscope; b. transmission electron microscope [3].

The ultimate size and V_f of the γ' particles can be controlled by varying the rate at which the material is cooled after solidification. Fig. 5 illustrates the effect of cooling rate during solidification of IN-100 superalloy on V_f and size of γ' particles. It is obvious that slower cooling provides not only higher V_f , but also smaller γ' particles. Superalloy engine components are strongest when they contain a high proportion (about 60 vol.%) of very small γ' particles.

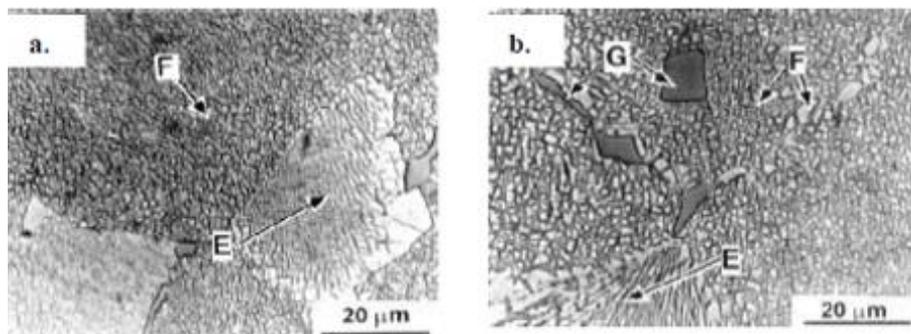


Fig. 5. Optical microscope. The effect of cooling rate during solidification of superalloy IN-100. (a) Slow cooling rate; (b) fast cooling rate. E- $\gamma + \gamma'$ eutectic; F- γ' particles; G-MC carbides [3].

Nickel-based superalloys, particularly those with high V_f of the γ' phase, generally retain useful strength at temperatures up to 900 °C (Table 3). In gas-turbine aircraft engines, heat resistant nickel-based alloys make up compressor blades in sections where the air is at its highest temperatures and pressures (the sections near the combustion chamber). Turbine blades in the sections closest to combustion chamber, where the exhaust gases are hottest, are also made of nickel-based superalloys.

Table 3. Change of Tensile Properties of Some Superalloys for Casting Application.

Alloy	Tensile properties	Temperature, °C					
		20	340	540	650	760	870
IN-713LC	R _m , MPa	897	897	897	1082	953	752
	A, %	15	14	11	11	11	11
IN-100	R _m , MPa	1014	1072	1092	1111	1070	828
	A, %	9	9	9	6	6.3	6
Mar-M200	R _m , MPa	932	942	946	953	932	741
	A, %	7	6	5	4	3.5	4

Choice and application of superalloys predominantly depend on their properties. Taking into account this reason, turbine blades and disks of aircraft turbojet engine are made of nickel-based superalloys. However, in nickel-based turbine blades, high-temperature exposure may produce a considerable microstructural change that might be the cause of serious deterioration of mechanical properties. The change of microstructure during annealing at 1200 °C is shown in Fig. 6.

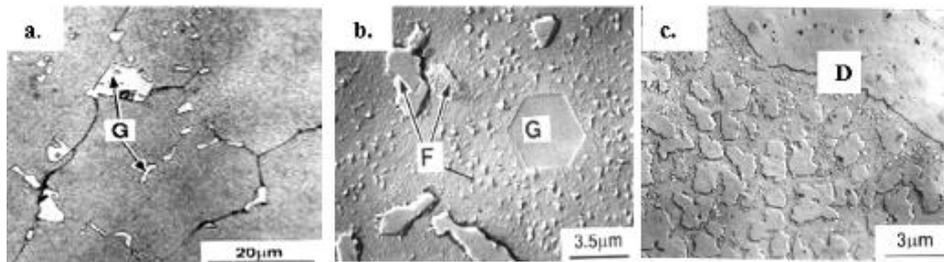


Fig. 6. Microstructure of IN-100 annealed at 1200 °C for 4h. (a) Optical microscope; (b,c) transmission electron microscope. F- γ' particles; G-MC carbides [4].

Blocky plate-like carbides (G) with rectangular edges can be seen at grain boundaries, while smaller carbides appear transgranularly. V_f of the γ' particles significantly decrease. A γ' -denuded zone exists near the grain boundary (D in Fig. 7c). The effect of temperature on V_f and the diameter of the γ' particles ($D_{\gamma'}$) is shown in Fig. 7 a,b, respectively. As temperature increases both V_f and $D_{\gamma'}$ significantly decrease.

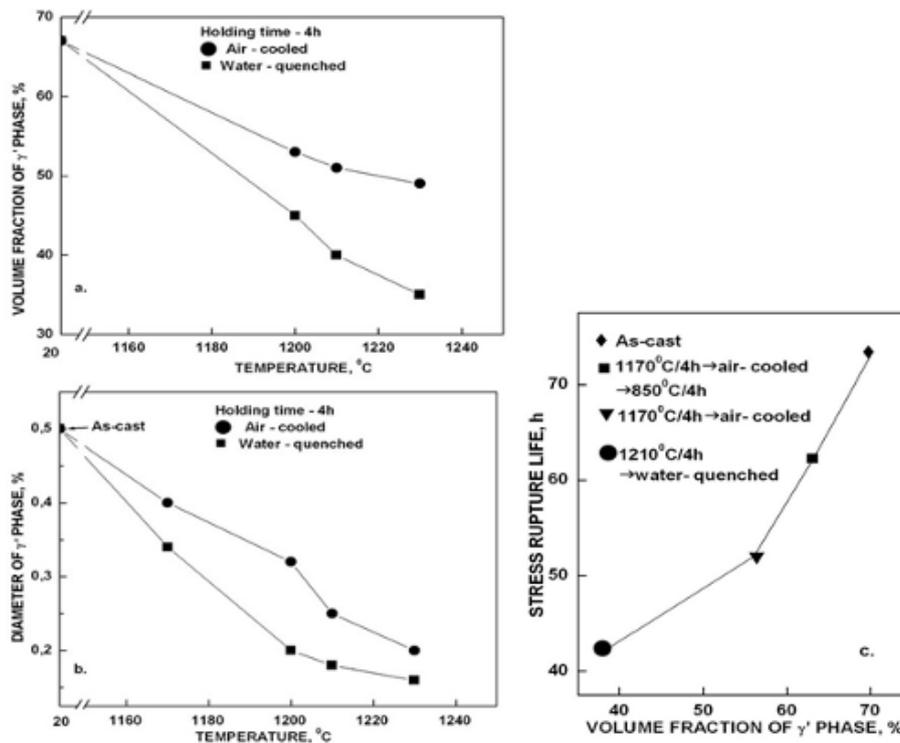


Fig. 7. Effect of annealing temperature on (a) volume fraction and (b) the diameter of the γ' particle; (c) correlation between stress rupture life and volume fraction of the γ' phase [4].

In the same time this decrease is more pronounced when the higher cooling rate was applied (water quenching vs. air cooling). The variation of creep resistance (stress rupture life) at 950 $^{\circ}\text{C}$ as a function of V_f is plotted in Fig. 7c. The increase in rupture life indicates that V_f plays an important role in the creep resistance. The decrease of creep resistance with temperature may be ascribed to the lower V_f which is a result of dissolution of γ' particles in the matrix.

Directional and single crystal solidification. At least as important as the advanced alloys themselves are advanced techniques for processing metals. These techniques enable metallurgist to shape and form samples of well-known alloys in ways that were never before possible.

One of the most important advanced processing techniques is called directional solidification. Contrary to the polycrystalline solidification, in directional solidification the mold is preheated to a temperature roughly equal to the molten metal; the bottom section of the mold is attached to a water-cooled “chill-plate”. The mold is held in a “hot zone” surrounded by a system of insulated heat baffles (Fig. 8a).

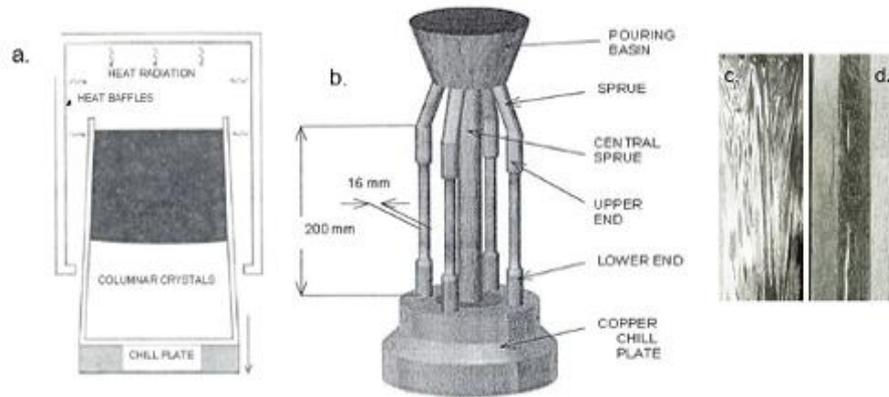


Fig. 8. Directional solidification of IN-939* superalloy. (a) Vacuum furnace with copper chill plate; (b) arrangement of directionally cast samples; (c,d) optical macrostructure of longitudinal section of castings, $\times 1$: lower end near the chill plate and upper end, respectively [5].

The melt is poured into the mold and begins to crystallize in the region of chill plate. The entire mold is then slowly lowered and withdrawn, bottom first, from the hot zone (Fig. 8b). Typically, many small individual crystals form and randomly grow at the copper chill plate together with extended columnar zone of grains growing normal to chill plate (Fig. 8c).

The final result is a sample made up of several long, columnar parallel grains with roughly the same most favorable orientation, i.e. $\langle 100 \rangle$ (Fig. 8d).

A similar procedure can produce single crystal castings with no grain boundaries at all. To produce a single crystal, a melt is poured into a ceramic mold that has a “pig tail”- shaped selector between the chill plate and the upper part of the mold (Fig. 9a). As the mold is withdrawn from the heat baffles (Fig. 9b), columnar grains begin to grow, but the selector is so narrow that only one of the crystals will grow through it (Fig 9c). Even as the mold widens above the selector, that crystal, becoming larger in diameter, is the only one to grow into the mold, and so the final sample (which is formed in the upper part of the mold) will be made of a single crystal with a characteristic dendritic structure (Fig. 9d).

*IN-939 (trade mark of International Nickel Ltd.) is a high Cr and Co series superalloy designed for blades and vanes of marine and land-based turbines.

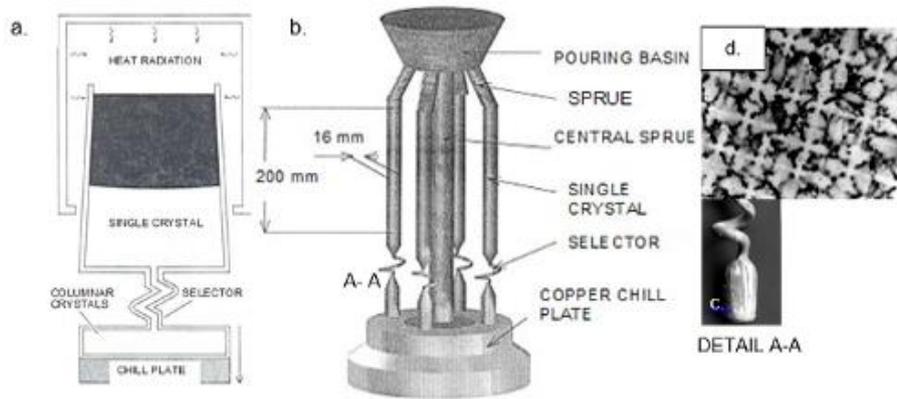


Fig. 9. Single crystal solidification of IN-939 superalloy. (a) Vacuum furnace with the copper-chill plate and the “pig tail” selector; (b) arrangement of single crystal castings; (c) macrostructure of “pig tail” selector, $\times 0.5$; (d) optical micrograph of single crystal structure [5].

Superalloy turbine blades with different microstructures are shown in Fig. 10. Standard casting (Fig. 10a) is made up of many crystals randomly oriented; in directionally solidified blade (Fig. 10b) columnar grains are parallel to the vertical axis of the blade and the number of grains is largely reduced; single crystal blade (Fig. 10c) has no grains.

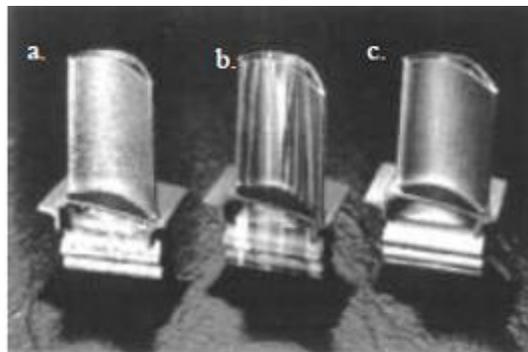


Fig. 10. Turbine blades produced by different casting technologies.

The results of stress-rupture life testing of IN-939 superalloy (Fig. 11) illustrate the dramatic increase of the resistance to creep when the number of grain boundaries is reduced and parallel to uniaxial stresses or, even, completely eliminated.

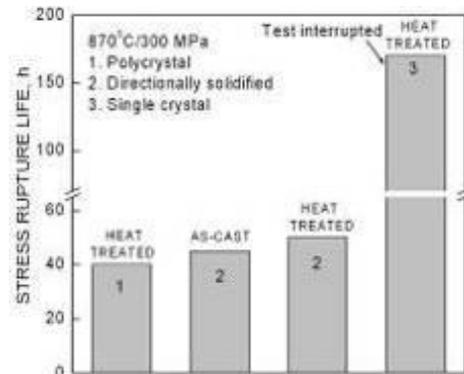


Fig. 11. IN-939. Stress-rupture life of polycrystal, directionally solidified and single crystal castings [6].

The increased V_f of the γ phase during heat treatment increases the stress-rupture life. The stress-rupture life of the single crystal castings was much longer (the tests were discontinued after 170h) than the stress-rupture life of either directionally solidified or, especially, the conventionally cast material. This result which shows longer stress-rupture life of single crystal may be explained as a consequence of the absence of grain boundaries as “weak locations” in the structure.

The values of stress-rupture life regarding the single crystal of IN-939 castings are at least several times higher than values reported in the literature.

Cobalt-based superalloys

Nickel-based superalloys have limitations at very high temperatures, and so components in the combustion chamber, where the temperature may reach as high as 1100 °C, are usually made of cobalt-based alloys.

The cobalt-based superalloys (Table 4) are not as strong as nickel-based superalloys, but they retain their strength up to higher temperatures. They derive their strength largely from a distribution of refractory metal carbides (combinations of carbon and metals such as Mo and W), which tend to collect at grain boundaries (Fig. 12).

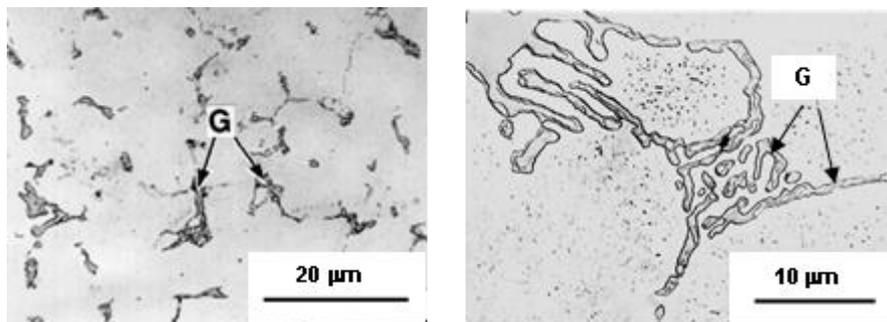


Fig. 12. Optical micrograph of Haynes-25. G-mainly M_6C carbides [7].

This network of carbides strengthens grain boundaries and alloy becomes stable nearly up to the melting point. In addition to refractory metals and metal carbides, cobalt superalloys generally contain high levels of Cr to make them more resistant to corrosion that normally takes place in the presence of hot exhaust gases. The Cr atoms react with oxygen atoms to form a protective layer of Cr_2O_3 which protects the alloy from corrosive gases. Being not as hard as nickel-based superalloys cobalt superalloys are not so sensitive to cracking under thermal shocks as other superalloys. Co-based superalloys are therefore more suitable for parts that need to be worked or welded, such as those in the intricate structures of the combustion chamber.

Table 4. Chemical Composition of Some Cobalt-Based Superalloys.

Alloy	C	Mn	Si	Cr	Ni	Mo	W	Fe	Co
X-45	.25	.5	.9	25	10	-	7.5	<2	bal
X-40	.5	.5	.9	25	10	-	7.5	<2	bal
FSX-414	.35	.5	.9	29.5	10	-	7.5	<2	bal
WI-52	.45	.4	.4	21	-	-	11	2	bal
Haynes -25	.1	1.2	.8	20	10	-	15	<3	bal
F-75	.25	.5	.8	28	<1	6	<.2	<.75	bal
Haynes Ultimet	.06	.8	.3	25	9	5	2	3	bal
Co 6	1.1		.8	29	<3	<1.5	5.5	<3	bal

Aero and land turbines. Cobalt superalloys are well-suited to high temperature creep and fatigue resistant non-rotating applications where stress levels are lower than for rotating components. For this reason, turbine vanes and other static non-rotating components are frequently designed in cobalt alloys. A somewhat lower coefficient of thermal expansion and better thermal conductivity than the nickel superalloys make cobalt alloys good candidates for applications where thermal fatigue is a critical design issue. Due to long service life requirements, land based casting specifications are becoming progressively more stringent (more rigorous than for similar aero counterparts in some cases).

Surgical implants. The alloy under the proprietary name Vitallium[®] has been known since the '30's of the last century. Today, this alloy is used for orthopaedic implants, most notably as artificial hips and knees. The alloy is generically referred to by its ASTM designation F-75 and contains 29% Cr and 6% Mo. While the ASTM specification limits carbon to 0.35%, implant manufacturers have opted for lower levels of carbon and an intentional alloying with nitrogen. This addition of nitrogen has allowed Co-Cr-Mo alloy to achieve high levels of strength with good ductility and

without sacrificing corrosion resistance and bio-compatibility. Co-Cr-Mo implants may be produced by casting, forging or powder metallurgy technology.

Titanium-based alloys

The high strength, low weight, outstanding corrosion resistance possessed by titanium and titanium alloys have led to a wide and diversified range of successful applications which demand high levels of reliable performance in aerospace, automotive, chemical plant, power generation, oil and gas extraction, sports and other industries, as well as in surgery and medicine.

Compared to nickel and cobalt-based superalloys, titanium-based alloys are far less dense possessing a higher ratio of strength to weight for temperatures below 500 °C. Titanium alloys are weakness at temperatures less than half their melting point, whereas superalloys maintained their strength about seven or eight-tenths their melting point. In some applications high strength and consistency at high temperatures are not crucial, and the weight of each component becomes a greater consideration. In the section of gas-turbine engine where temperatures and pressures are moderate, titanium-based alloys are often the most appropriate.

Important characteristic of titanium-based materials is the reversible transformation of the crystal structure from α hexagonal-close-packed (h.c.p.) to β body-centered-cubic (b.c.c.) structure when the temperature exceeds certain level, known as a transus temperature. This allotropic behavior, which depends on the chemical composition of the alloy, allows complex variation in microstructure and more diverse strengthening than other non-ferrous alloys.

The demand for the use of titanium and its alloys in many areas of military and civil applications has been increased over the past years by the necessity for weight reductions. Due to the high cost of titanium, the use of net-shape or near-net-shape technologies receive an increasing interest considering the large cost saving potential of this technology in manufacturing parts of complex shapes. Investment (precision) casting is by far the most fully developed net-shape technology compared to powder metallurgy, superplastic forming and rolling. The main difficulties in production high quality titanium and titanium alloy castings are: the high melting point, the extremely high reactivity of melt with solids, liquids and gases at high temperatures. For these reasons, traditional casting techniques and materials cannot be used both for melting and molding operations. In addition, melting and pouring have to be performed under vacuum or inert gas. The production of investment molds for titanium casting is similar to the production of investment molds for ferrous and superalloys castings except for some very important differences. The major difference is in the investment slurry formulation. Due to a high reactivity of molten titanium a special attention must be paid to the chemical composition of ceramic molds. Investment molds for titanium castings must be made of special high-stability refractories such as zirconia, thoria and yttria.

The most widely used titanium alloy is one containing (in wt.%): 6 Al, 4 V, the rest is titanium. This alloy has an excellent combination of strength, toughness and good corrosion resistance and finds uses in aerospace applications, pressure vessels, aircraft-turbine and compressor blades and discs, turbochargers, surgical implants (Fig. 13) etc.

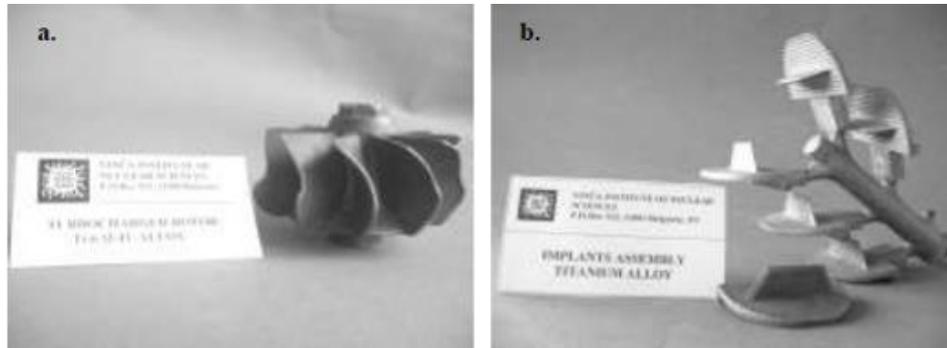


Fig. 13. Turbocharger rotor (a) and surgical implant device (b) made of Ti-6Al-4V alloy via technology of investment casting [8].

Al stabilizes the α phase, while V stabilizes the β phase. When Ti-6Al-4V is slowly cooled from the β region, α begins to form below the β transus temperature that is about 980 °C. The kinetics of $\beta \rightarrow \alpha$ transformation upon cooling strongly influences properties of this alloy. The effect of cooling rate on the microstructure of Ti-6Al-4V is shown in Fig. 14.

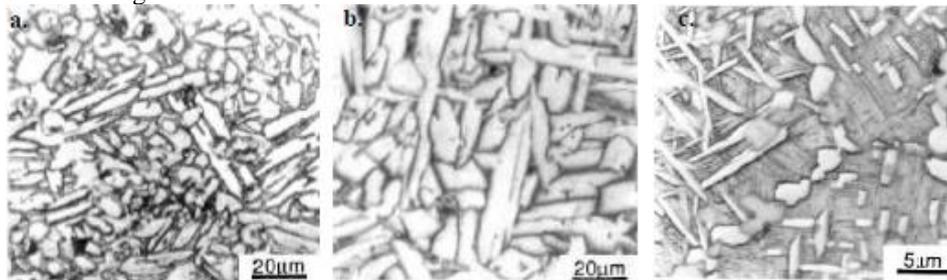


Fig. 14. Optical micrograph of Ti-6Al-4V alloy. (a) As-cast; (b) furnace-cooled from 900 °C; (c) water-quenched from 900 °C [9].

Surgical implants. The strength-to-density ratio of Ti-6Al-4V is better than any other surgical implant material (Fig. 15). Both pure titanium and Ti-6Al-4V alloy are widely used in prosthetic devices, the choice depending on the functional requirements of material. An additional advantage of these materials is their compatibility with imaging techniques such as computed tomography, scanning and magnetic resonance imaging. The good strength-to weight ratio, fatigue resistance and low modulus of elasticity of Ti-6Al-4V makes it one of the best alloys for implanting into bone and it is often used for the bone stems of modular artificial joints, as well as for other prosthetic devices.

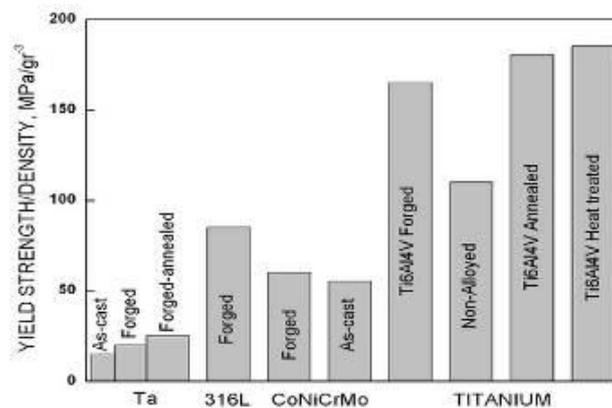


Fig. 15. Strength-to-density ratio of some alloys for medical application.

For the production of prototypes of surgical implants (hips and sholders), which have a rather complicated shape, a conventional investment casting “lost-wax” procedure was performed using proprietary “self-supporting” ZrO₂-based ceramic shell molds [10]. Ceramic shell molds for sholders and hips are shown in Fig. 16.

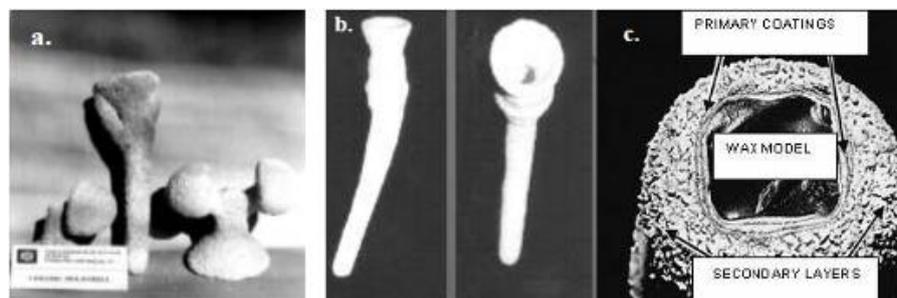


Fig. 16. Ceramic “self-supporting” shell molds. (a) Sholders - sockets and stems; (b) hips; (c) cross-section of mold [10].

Some prototypes of precision cast sholders and hips are shown in Fig. 17.

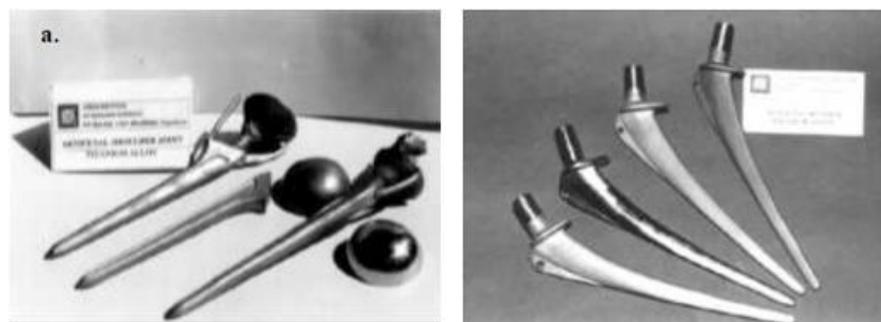


Fig. 17. Precision cast prototypes of surgical implants. (a) Sholders - sockets and stems; (b) hips [10].

Concluding remarks

The paper represents an overview of the results implemented by a group of authors working on the research and development of high-temperature materials based on nickel, cobalt and titanium alloys. These results were accomplished in the Department of Materials Science, "Vinča" Institute, through different projects.

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