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SUMMARY

A wrought nickel-base superalloy based on the Ni-Cr-W system was developed for high-temperature applications. The new alloy is solid solution and carbide strengthened. It is essentially free of cobalt, and it resists the formation of detrimental intermetallic compounds after prolonged exposure to elevated temperatures. Various mechanical, oxidation and physical properties of the new alloy were measured, and the microstructural features were characterized. These were compared with those of other solid solution-strengthened superalloys. Also, the fabricability of the alloy was evaluated. A number of advantages of the new alloy are defined.

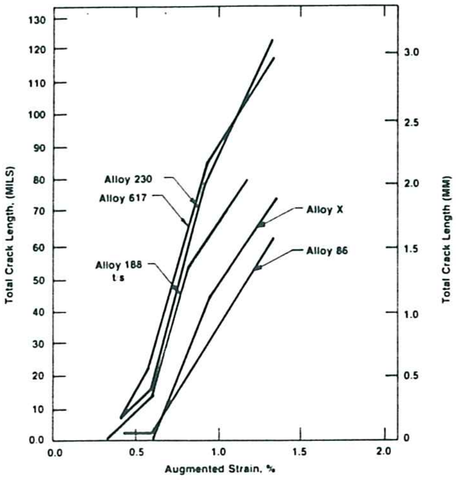

Figure 1. Susceptibility to heat-affected zone cracking as a function of strain (TIG-A-MA-JIG test results).

INTRODUCTION

Over the past three decades, superalloys have played significant roles in advanced technological applications particularly in the aircraft and power generation fields, e.g., References 1 and 2. Solid solution-strengthened nickel- and cobalt-base alloys with unique combinations of mechanical strength, environmental resistance, and fabricability, have been of particular importance in the manufacturing of combustor components of gas turbine engines. This is because alloys based on precipitation hardenable systems do not usually have the workability and weldability characteristics displayed by solid solution-strengthened alloys.

Since the occurrence of the cobalt crisis in the late 1970s, a great deal of attention has been focused on the role of strategic elements in superalloys with emphasis on cobalt. Most of the effort has been devoted to reducing the cobalt content of existing alloys while maintaining an acceptable level of properties as demonstrated by the COSAM program.[13] It is, however, more desirable to develop new alloys which are free of cobalt. Research efforts at Cabot Corporation over the past few years have led to the development of a new nickel-base superalloy which is essentially free of cobalt and with significantly better combinations of properties than HASTELLOY® alloy X and NIMONIC® alloy 86. Also, the properties of this alloy are comparable to or better than those of nickel-base alloys containing significant amounts of cobalt, e.g., INCONEL® alloy 617, and approach the properties of cobalt-base alloys, e.g., HAYNES® alloy No. 188. The new alloy is known as HAYNES® alloy 23. All the mechanical property data presented in this paper were derived from sheet products of production heats [30,000-lb (13,635-kg)].

CHEMICAL COMPOSITION

Alloy 230 is primarily a solid solution and carbide strengthened Ni-Cr-W alloy. Its nominal chemical composition is given in Table I in comparison with the compositions of other solid solution-strengthened alloys. Tungsten was selected as the primary source of solid solution strengthening because of its larger atomic size and lower diffusivity in nickel as compared to molybdenum. Also, tungsten considerably reduces the stacking fault energy of nickel (e.g., Reference 4) which provides for restricted cross-slip of glide dislocations. The excellent oxidation resistance of the alloy was achieved by a combination of chromium and minor but critical additions of lanthanum, silicon, and manganese which are known to promote stable and tenacious protective oxides. Neither iron nor cobalt are essential, however, a maximum level of 3 wt.% of each was set to establish a production tolerance of their presence. In order to prevent the precipitation of detrimental intermetallic compounds after prolonged exposure to elevated temperatures, the chemistry of each heat is controlled by utilizing the electron vacancy number (Nv) approach.[5]

FABRICABILITY

Good workability and weldability are essential fabrication characteristics in the manufacturing of combustor components of gas turbine engines. Alloy 230 has a good room temperature ductility as demonstrated by the

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Table I: Nominal Chemical Compositions, wt.%

Alloy	Ni	Co	Cr	Mo	W	Fe	Si	Mn	C	Al	Others
X	bal	1.5	22	9	0.6	18.5	1.0 *	1.0 *	0.10	—	—
617	bal	12.5	22	9	—	1.5	0.50	0.50	0.07	1.20	0.3 Ti
86	bal	—	25	10	—	5.0 *	1.0 *	1.0 *	0.05	—	0.015 Mg 0.03 Ce
188	22	bal	22	—	14.0	3.0*	0.35	1.25*	0.10	—	0.04 La
230	bal	3.0*	22	2	14.0	3.0*	0.40	0.50	0.10	0.30	0.03 La

*Maximum

Table II: Room-Temperature Tensile Properties and Olsen Cup Depths

Alloy	0.2% YS, ksi (MPa)	UTS, ksi (MPa)	Elongation in 2 in. (50.8mm), %	Olsen Cup Depth, in. (mm)
X	55 (380)	111 (765)	44	0.484 (12.3)
617	49 (340)	107 (740)	60	0.476 (12.1)
86	53.5 (370)	114 (785)	55	0.505 (12.8)
188	69.5 (480)	138 (950)	53	0.490 (12.4)
230	57 (395)	126 (870)	48	0.460 (11.7)

tensile properties and Olsen cup depths given in Table II in comparison with the ductilities of other alloys. This permits the alloy to be fabricated by the standard techniques used for nickel- and cobalt-base alloys. Hot working can be easily accomplished provided the alloy is held at 2150°F (1175°C) for a time sufficient to bring the entire workpiece to temperature before forging or rolling. All hot- or cold-worked parts are solution heat treated at a temperature in the range 2050-2250°F (1120-1230°C) depending on the particular application and then rapidly cooled to restore optimum ductility. The resulting grain size is ASTM No. 4 or finer which achieves a good compromise between the tensile and creep strengths.

As indicated earlier, solid solution-strengthened superalloys have better weldability characteristics as compared to alloys based on precipitation hardenable systems. The common welding techniques of superalloys include tungsten-inert-gas (TIG), metal-inert-gas (MIG), and electron beam welding. Component fabrication procedures often lead to the presence of mechanical strains which promote heat-affected zone (HAZ) cracking during welding. Resistance to HAZ cracking is therefore an important property which needs to be characterized. The susceptibility to HAZ cracking can be evaluated as a function of imposed mechanical strain in sheet material by using a test known as the spot varestraint TIG-A-MA-JIG test.[6] Figure 1 shows the results of TIG-A-MA-JIG tests conducted on alloy 230 and other solid solution-strengthened alloys. It can be seen that the resistance of alloy 230 to HAZ cracking is similar to that of alloys 188 and 617.

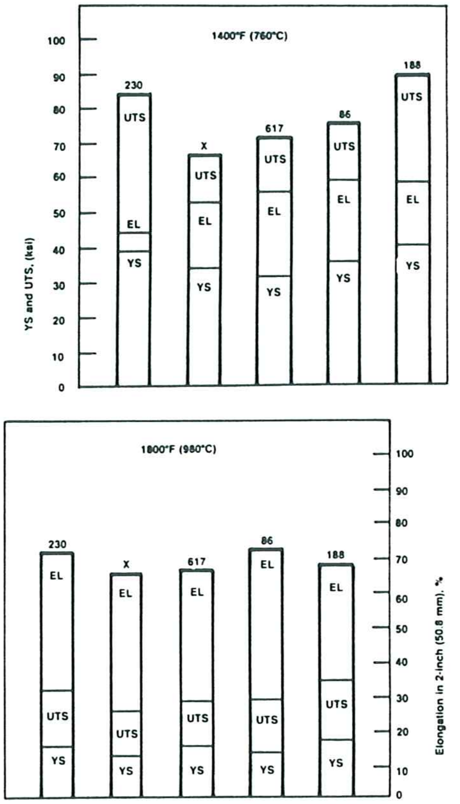


Figure 2. Tensile properties at 1400°F (760°C) and 1800°F (980°C).

MECHANICAL STRENGTH

The most important mechanical properties which allow superalloys to tolerate the in-service conditions include: tensile, creep-rupture, and fatigue strengths in the temperature range 1200°-1800°F (650°-980°C).

Tensile Strength

Figure 2 shows the tensile properties of alloy 230 at 1400°F (760°C) and 1800°F (980°C) in comparison with those of other alloys. It can be seen that alloy 230 has a tensile strength which approaches that of alloy 188. By noting the differences between the yield and ultimate strengths, it can be concluded that alloys 230 and 188 have similar strain-hardening characteristics. Cobalt-base alloys are generally known for their low stacking fault energy which is one of the factors that can lead to a higher strain hardening rate.[7] The similarity of alloy 230 to alloy 188 in the strain-hardening characteristics may be attributed to the effectiveness of tungsten in lowering the stacking fault energy of nickel.[4]

Creep-Rupture Strength

One of the important parameters in designing alloys for high-temperature applications is the low strain creep strength. Also of importance is the creep-rupture life. Figure 3 shows Larson-Miller plots of the 0.5% creep and rupture strengths of alloy 230 in comparison with other alloys. It can be seen that the 0.5% creep strength of alloy 230 is significantly higher than that of alloy X. The difference between the creep strengths of these two alloys varies from about one Larson-Miller parameter at lower temper-

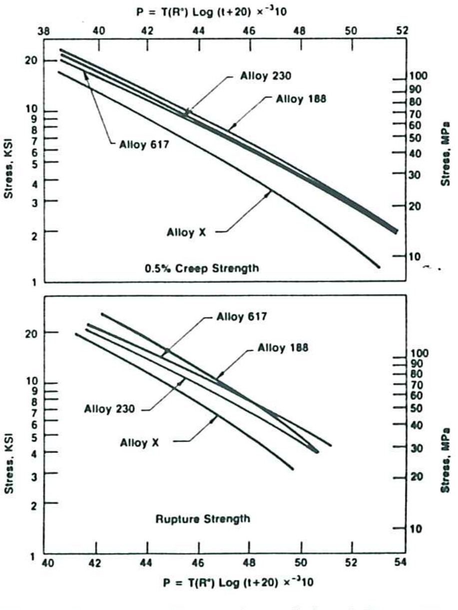


Figure 3. Larson-Miller plots of the 0.5% creep and rupture strengths.

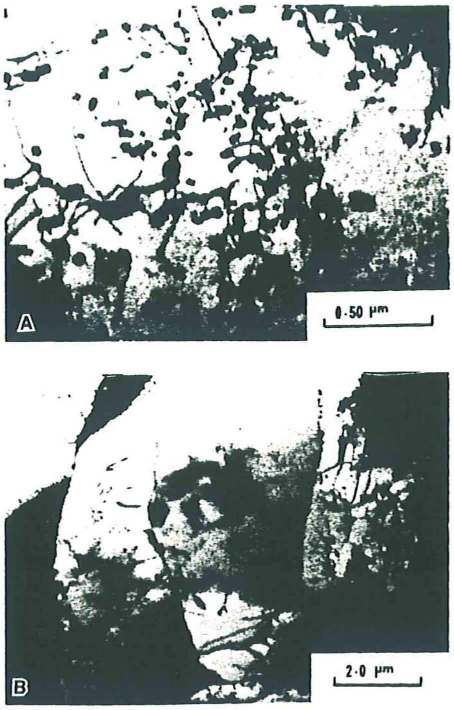


Figure 4. Bright-field TEM micrographs showing typical steady-state creep substructure in a sheet sample of alloy 230 crept at 1700°F/6 ksi (925°C/40 MPa); (a) fine $M_{23}C_6$ carbide particles at dislocations, and (b) subgrain structure.

atures to 1½ parameters at higher temperatures. Also, the 0.5% creep strength of alloy 230 is similar to that of alloy 617 which contains nominally 12.5 wt.% Co, and approaches that of the cobalt-base alloy 188. As to the rupture-strength, alloy 230 is also significantly stronger than alloy X and approaches the strengths of alloys 617 and 188. It should be noted, however, that alloy 617 has a larger grain size.

The high creep strength of alloy 230 is partially attributed to the precipitation of fine particles of $M_{23}C_6$ carbide on slip dislocations. Characteristic steady-state substructures are shown in the transmission electron micrographs of Figure 4. Fine $M_{23}C_6$ carbide precipitates at dislocations can be seen in Figure 4a. A subgrain structure is shown in Figure 4b.

Fatigue Strength

The operating conditions in a gas turbine engine involve thermal cycling which can lead to thermal fatigue failure. Some preliminary uniaxial strain-controlled low-cycle fatigue tests were conducted at 1600°F (870°C) to assess the high-temperature fatigue resistance of alloy 230. Uniform gage section specimens were machined from 0.5-in. (12.5 mm) thick plate material in the solution-annealed condition. The tests were conducted using a fully reversed triangular strain wave form and a strain rate of 5×10^{-9}/s. Figure 5 illustrates the results obtained for alloy 230 along with comparative data for alloys X and 188. A comparison of these results indicates that alloy 230 exhibits low-cycle fatigue resistance equivalent to that of alloy X in the low total strain regime which is of practical significance in design. In this same regime, alloy 188 can be seen to have significantly higher fatigue lives. This implies that, cobalt-base alloys are superior to nickel-base alloys in low-cycle fatigue resistance. Studies are currently being done to determine if a similar behavior occurs in the case of thermal fatigue.

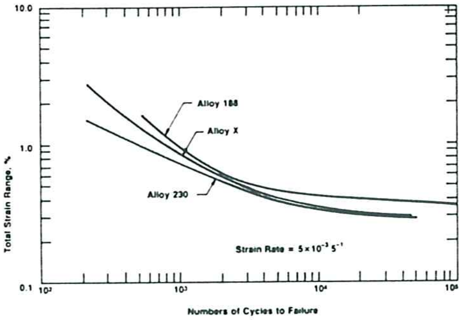
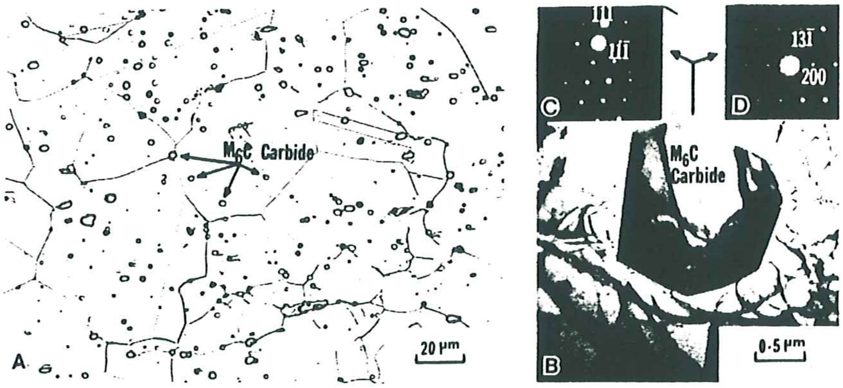


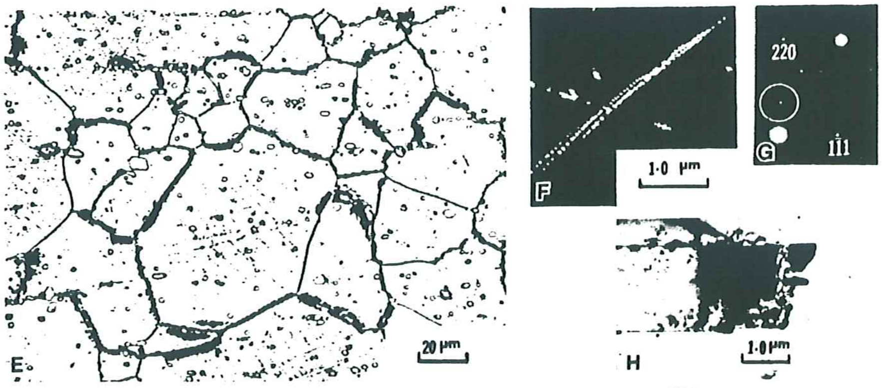
Figure 5. A comparison of the low-cycle fatigue lives of alloys X, 188 and 230.

MICROSTRUCTURAL FEATURES

The matrix of alloy 230 is a face-centered cubic solid solution with lattice constant of 3.6Å (0.36 nm). Usually the average grain size is ASTM No. 4 or finer. In the solution-annealed condition, a relatively small amount of a tungsten-rich carbide is dispersed in the matrix as shown in the optical micrograph of Figure 6a. This carbide is referred to as "primary" in order to distinguish it from other carbides which precipitate after exposure to elevated temperatures and are designated as "secondary." The primary carbide in alloy 230 was identified by x-ray and electron diffraction to be of the M_6C-type [(fcc with a lattice constant of 11.08Å (1.108



(a-d) in the solution-annealed condition



(e-h) after 1000 hours of exposure at 1400°F (760°C)

Figure 6. Typical microstructural features of alloy 230; (a) optical micrograph; (b) TEM micrograph showing M_6C carbide particle, (c-d) selected area electron diffraction patterns derived from the particle in b; (c) $[011]_{fcc}$, (d) $[013]_{fcc}$, (e) optical micrograph; (f) dark-field TEM micrograph formed with the encircled $M_{23}C_6$ carbide reflection in g; (h) $M_{23}C_6$ carbide particles at a twin boundary.

nm)]. An example is shown in the bright-field transmission electron micrograph and corresponding diffraction patterns of Figures 6b-d. Exposure of alloy 230 to temperatures below approximately 2100°F (1150°C) results in the precipitation of Cr-rich $M_{23}C_6$ carbide. Transmission electron microscopy and diffraction studies conducted on samples exposed for up to 1000 hours at temperatures in the range 1200°-1800°F (650°-980°C) have revealed that the only secondary precipitate in alloy 230 is the $M_{23}C_6$ carbide. An example is given in Figure 6e which shows a characteristic optical microstructure of the secondary $M_{23}C_6$ carbide precipitates after 1000 hours of exposure at 1400°F (760°C). Preferred nucleation sites of this carbide include grain boundaries (Figure 6e) and pre-existing dislocations and twin boundaries as illustrated by the transmission electron micrographs and diffraction patterns of Figure 6f-h.

The precipitation characteristics of alloy 230 described above resemble those of alloy 617[8] and also alloy 86 but contrast those of alloy X and alloy 188. In alloy X, σ and μ phases precipitate[9] and Laves phase precipitates in alloy 188.[10] These topologically close-packed phases are known to have detrimental effects on mechanical properties.[11] The resistance of alloy 230 to the precipitation of such phases is reflected by a high retained room-temperature tensile elongation following prolonged exposure to elevated temperatures as described below.

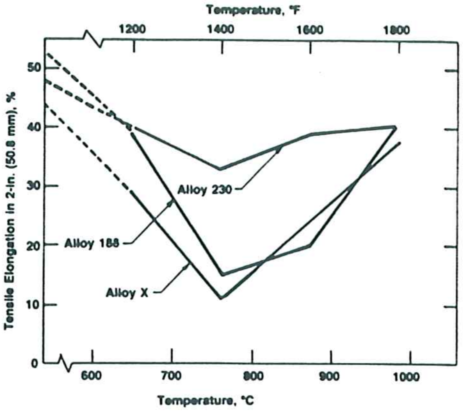


Figure 7. Effect of 1000 hours of exposure at various temperatures on the room temperature tensile elongations of alloys X, 188 and 230.

EFFECT OF PROLONGED EXPOSURE TO ELEVATED TEMPERATURES ON DUCTILITY (THERMAL STABILITY)

The retained room-temperature ductility of superalloys after prolonged exposure to elevated temperatures is important in connection with repair operations. Such operations involve cold straightening which requires sufficiently high-ductility level. Figure 7 shows the retained room temperature tensile elongation of alloy 230 after 1000 hours of exposure to temperatures in the range 1200°-1800°F (650°-980°C) along with comparative data for alloys X and 188. It can be seen that the thermal stability of alloy 230 is significantly better than that of alloys X and 188 due to its greater resistance to the precipitation of detrimental intermetallic compounds. In this regard, alloys 617 and 86 behave in a similar fashion to alloy 230.

OXIDATION RESISTANCE

Gas turbine combustor alloys must be capable of withstanding the hostile environments created by the high-velocity gases under operating conditions which involve temperature cycling. These conditions were simulated in laboratory dynamic oxidation tests using a burner rig employing No. 2 fuel oil with an air-to-fuel ratio of about 52:1 to achieve a combustion gas velocity of Mach 0.3. During testing, the samples were cycled out of the hot zone every 30 min, forced to air cool to a temperature below about 500°F (260°C) in two minutes,and then re-inserted to the hot zone. Tested samples were evaluted in terms of metal loss (oxide spallation and volatization) and internal oxidation using optical metallography. The sum of these two parameters provides a measure of the total amount of metal affected by the oxidation attack.

Figure 8 shows the results obtained for sheet samples of alloy 230 tested for up to 300 hours at 2000°F (1095°C) in comparison with the results

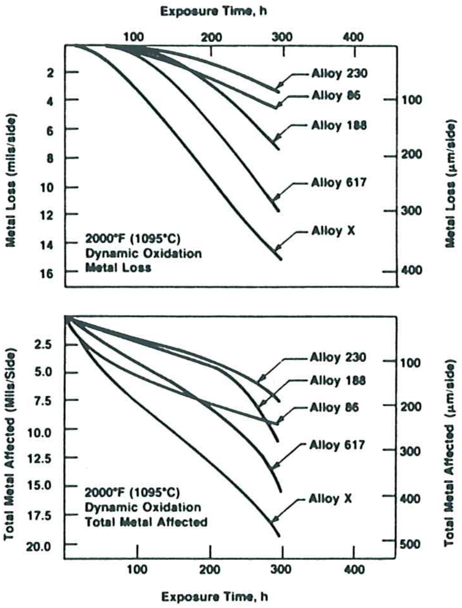


Figure 8. Dynamic oxidation properties at 2000°F (1095°C).

Table III: Density and Mean Coefficients of Thermal Expansion 70°F (20°C) to the Indicated Temperatures, 10^{-6}/°F (10^{-6}/°C)

	Temperature, °F (°C)								Density	
Alloy	1200	(650)	1400	(760)	1600	(870)	1800	(980)	lb/in.^{3}	(kg/m^3)
X	8.7	(15.5)	8.8	(15.8)	9.07	(16.2)	9.3	(16.6)	0.297	(8220)
617	8.06	(14.4)	8.5	(15.1)	8.8	(15.7)	9.07	(16.2)	0.302	(8291)
86	8.06	(14.4)	8.3	(14.9)	8.8	(15.7)	9.2	(16.4)	0.305	(8540)
188	8.7	(15.5)	9.07	(16.2)	9.5	(16.9)	10.0	(17.8)	0.324	(8968)
230	8.2	(14.6)	8.3	(14.9)	8.7	(15.5)	9.0	(16.0)	0.319	(8830)

Table IV: Dynamic Moduli of Elasticity as Functions of Temperature, 10^3 ksi (GPA)

	Temperature, °F ('°FC)							
Alloy	1200	(650)	(1400	(760)	1600	(870)	1800	(980)
X	22.0	(154)	21.0	(145)	20.0	(137)	18.0	(127)
617	24.5	(169)	23.0	(161)	22.0	(151)	20.0	(141)
86	25.0	(172)	24.0	(163)	22.0	(154)	21.0	(144)
188	26.0	(181)	25.0	(172)	24.0	(163)	22.0	(154)
230	25.0	(174)	24.0	(166)	23.0	(159)	22.0	(151)

obtained for the other alloys. It can be seen that alloy 230 exhibits greater resistance to oxidation rather than the other alloys tested. Noting that all of these alloys contain a nominal of 22 wt.% Cr, the greater resistance of alloy 230 to oxidation attack may be due to the synergestic effects of chromium, nickel, and the effective minor elemental additions of lanthanum, silicon, and manganese.

PHYSICAL PROPERTIES

Important physical properties of alloys for high-temperature applications include density, coefficient of thermal expansion, and dynamic elastic modulus. Table III shows the densities and the mean coefficients of thermal expansions of alloy 230 in comparison with other alloys. As can be seen, alloy 230 exhibits a relatively low coefficient of thermal expansion over the temperature range 1200°-1800°F (650°-980°C) is given in Table IV. It can be seen that as the temperature is increased from 1200°F to 1800°F, the modulus of alloy 230 approaches that of alloy 188 and becomes higher than that of the other alloys.

CONCLUDING REMARKS

A new solid solution and carbide strengthened nickel-base superalloy which is essentially free of cobalt was developed for high-temperature applications. The new alloy can be fabricated by the standard techniques used for nickel- and cobalt-base superalloys, and it has an excellent combination of mechanical strength, oxidation resistance, thermal stability, and physical characteristics. Possible applications for the new alloy include flying and land-based gas turbines, high-temperature gas-cooled reactors, and high-temperature components in various process industries.

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ABOUT THE AUTHORS

Hani M. Tawancy, Engineering Associate, Technology Department, Cabot Corporation, Kokomo, Indiana 46901.

Dr. Tawancy received his MS and PhD in materials science from the University of California, Berkeley in 1973 and 1976, respectively. He has authored and co-authored several papers in the area of structure/property relationships of superalloys. He is a member of The Metallurgical Society of AIME.

Dwaine L. Klarstrom, Manager of Product Development, Technology Department, Cabot Corporation, Kokomo, Indiana 46901.

Dr. Klarstrom received his BS, MS, and PhD in metallurgical engineering from the University of Wisconsin-Madison, in 1965, 1966 and 1970, respectively. His areas of research have included brazing, thermomechanical processing, and high-temperature alloy development. He has authored and co-authored technical publications in a variety of research areas.

Michael F. Rothman, Group Leader for High-Temperature Alloys, Technology Department, Cabot Corporation, Kokomo, Indiana 46901.

Mr. Rothman holds a BS and MS in metallurgical engineering from the Polytechnic Institute of Brooklyn in 1967 and 1969, respectively. He has been active in the field of high-temperature metallurgy and materials, and he has authored numerous papers in the areas of superalloys and superalloy processing. He is a member of The Metallurgical Society of AIME.