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100+ YEARS OF WROUGHT ALLOY DEVELOPMENT AT HAYNES INTERNATIONAL

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Abstract

For over 100 years Haynes International has, through alloy development, provided innovative solutions to materials problems to its customers. In return, its customers, through advancements in technology, have posed more and more challenging materials problems. The tradition of innovation at Haynes International began with the invention/development of the Stellite-type alloys. Since then, many new alloys have been introduced, including entirely new alloy families. These include the solid-solution strengthened superalloys and their predecessors - the B-type (Ni-Mo) and C-type (Ni-Cr-Mo) alloys, as well as the wrought Ni-base alumina-formers, $Ni_2(Mo,Cr)$-strengthened alloys, and nitrogen dispersion strengthened (NDS) alloys. The purpose of this manuscript will be to provide an overview of the rich and ongoing history of wrought alloy development within the company. Particular emphasis will be placed on fabricable superalloys - which are in the same general category as 718 alloy, for which this conference is named.

Introduction

Today almost all products manufactured by Haynes International are conventional wrought products. That is, they have been produced through ingot metallurgy and some combination of hot/cold working. However, that has not always been the case. In the early days of the company castings were the primary product. In fact, the company was one of the pioneers of the investment cast process on a mass scale. It is estimated that during WWII more than 70% of supercharger buckets were cast by Haynes Stellite at its Kokomo, Indiana foundry [1]. Despite the rich history in cast products, this manuscript will focus only on wrought alloys developed by the company – and in particular, will focus mainly on alloys still produced today. There are 31 such alloys currently produced at Haynes International, both high-temperature and corrosion-resistant. The nominal compositions of these alloys are provided in Table I. Information on the invention/development of all of these alloys will be provided in this manuscript. However, because of the nature of this conference, only those alloys which can be defined as "fabricable superalloys" will be described in detail. Such alloys are developed for gas turbine engines, are typically Ni, Co, or Fe-Ni based, possess good creep strength and oxidation/corrosion resistance at elevated temperatures, and are readily hot/cold workable, weldable, and formable.

The history of alloy development at Haynes International can be divided into five chapters, generally tied to the overall history of the company. The key fabricable superalloys invented during each chapter will be briefly reviewed.

HAYNES, HASTELLOY, B-3, C-2000, C-22, C-22HS, G-30, G-35, ULTIMET, HYBRID-BC1, MULTIMET, HR-120, HR-160, HR-224, 214, 230, 242, 282, 556, and NS-163 are registered trademarks of Haynes International. 244 and HR-235 are trademarks of Haynes International. Stellite is a registered trademark of Kennametal Stellite.

Table I. Nominal Compositions[†] of Wrought Alloys Developed by Haynes International

Alloy	Ni	Co	Fe	Cr	Mo	W	Mn	Si	Al	Ti	C	B	Other
Nickel-Base Alloys													
B	Bal.	2.5*	5	1*	28		1*	1*			0.05*		0.3V
W	Bal.	2.5*	6	5	24	1*	1*	1*			0.12*		0.6*V
X	Bal.	1.5	18	22	9	0.6	1*	1*	0.5*	0.15*	0.10	0.008*	
N	Bal.	0.2*	4*	7	16	0.5*	0.8*	1*			0.06		
C-276	Bal.	2.5*	5	16	16	4	1*	0.08*			0.01*		
C-4	Bal.	2*	3*	16	16		1*	0.08*		0.7*	0.01*		
S	Bal.	2*	3*	16	15	1*	0.5	0.4	0.25		0.02*	0.015*	0.02La
G-30®	Bal.	5*	15	30	5.5	2.5	1.5*	0.8*			0.03*		2Cu, 0.8 Nb
214®	Bal.	2*	3	16	0.5*	0.5*	0.5*	0.2*	4.5	0.5*	0.04	0.01*	0.01Y, 0.1*Zr
230®	Bal.	5*	3*	22	2	14	0.5	0.4	0.3	0.1*	0.10	0.015*	0.02La
C-22®	Bal.	2.5*	3	22	13	3	0.5*	0.08*			0.01*		
HR-160®	Bal.	29	2*	28	1*	1*	0.5	2.75	0.4*	0.5	0.05		
242®	Bal.	1*	2*	8	25		0.8*	0.8*	0.5*		0.03*	0.006*	
D-205®	Bal.		6	20	2.5			5			0.03*		2Cu
C-2000®	Bal.	2*	3*	23	16		0.5*	0.08*	0.5*		0.01*		1.6Cu
B-3®	Bal.	3*	1.5	1.5	28.5	3*	3*	0.1*	0.5*	0.2*	0.01*		
G-35®	Bal.	1*	2*	33	8.1	0.6*	0.5*	0.6*	0.4*		0.05		
C-22HS®	Bal.	1*	2*	21	17	1*	0.8*	0.08*	0.5*		0.01*	0.006*	
HYBRID-BC1®	Bal.		1.25*	15	22		0.25*	0.08*	0.5*		0.01*		
282	Bal.	10	1.5*	20	8.5		0.3*	0.15*	1.5	2.1	0.06	0.005	
HR-224®	Bal.	2*	27.5	20	0.5*	0.5*	0.5*	0.3	3.6	0.3	0.05	0.004*	
244™	Bal.	1*	2*	8	22.5	6	0.8*	0.1*	0.5*		0.03*	0.006*	
Co-Base Alloys													
6B	2.5	Bal.	3*	30	1.5*	4	1.4	0.7			1		
25	10	Bal.	3*	20	1*	15	1.5	0.4*			0.10		
188	22	Bal.	3*	22		14	1.25*	0.35			0.10	0.015*	0.03La
ULTIMET®	9	Bal.	3	26	5	2	0.8	0.3			0.06		0.08N
NS-163®	8	Bal.	21	28			0.5*	0.5*	0.5*	1.3	0.10	0.015*	1 Nb
Fe-Base Alloys													
MULTIMET®	20	20	Bal.	21	3	2.5	1.5	1*			0.12		1 Nb, 0.15N
556®	20	18	Bal.	22	3	2.5	1	0.4	0.2		0.10	0.02*	0.6Ta, 0.02 Zr , 0.02La, 0.20N
HR-120®	37	3*	Bal.	25	1*	0.5*	0.7	0.6	0.1	0.2*	0.05	0.004	0.7 Nb, 0.20N

[†] All compositions in this manuscript are given in wt.% *Maximum

Haynes Stellite Company (1912 to 1920)

The origin of the present day Haynes International begins first with Elwood Haynes, a world-renowned inventor and metallurgist. The many pursuits and contributions of Mr. Haynes (automobiles, stainless steel, etc.) are well documented and make for interesting reading [1,2]. For the purposes of this manuscript, what is most relevant is his invention of a series of cobalt-base, wear-resistant alloys, known commercially as the Stellite® alloys (so-named from the Latin word for star, "Stella", due to the permanent star-like luster of the alloys). Mr. Haynes invented these alloys on his own using various makeshift laboratory facilities, including one in his own backyard in Kokomo, Indiana. Originally developed to produce fine cutlery, the Stellite alloys found widespread application as tool material for cutting, high speed machining, etc. The first patent for Stellite-type alloys was issued in 1907 and a subsequent pair of patent applications was submitted in 1912. Upon hearing in September of that year that these latter patents would be granted, Mr. Haynes founded the Haynes Stellite Company in Kokomo to manufacture and sell them. The unique properties of the Stellite alloys propelled the new company to grow, particularly during WWI where the use of Stellite cutting tools in the machining of munitions proved critical.

6B alloy While this alloy may not quite fit the definition of a fabricable superalloy as described above, some attention is due here since it is the oldest of the wrought alloys still produced by Haynes International. A member of the Stellite-type (Co-Cr-W) alloys, it has outstanding resistance to most types of wear. There is considerable difficulty in manufacturing the Co-Cr-W alloys through conventional hot/cold working methods, a consequence of their high carbon content and rapid work hardening rates. Therefore, most are normally produced as castings or through powder metallurgy. However, one composition (Co-28Cr-1.5W-1.15C) was amenable to hot working, albeit through a rather slow and tedious process. That composition is known as 6B alloy and was covered by one of Elwood Haynes original patents, see Table II. It can be produced in sheet, plate, and bar form. Applications include sleeves, bushings, bearings, valves and valve seats, saw blade, and turbine blade shields.

Table II. Wrought Alloys Developed from 1912 to 1920

Alloy	Inventor(s)	Location	U.S. Patent No.	Issue Date
6B	Elwood Haynes	Kokomo	1,057,423	1913

Union Carbide Years (1920 to 1969)

In 1920, the Haynes Stellite Company was sold to Union Carbide where it remained for almost 50 years. The name of the company was kept in place until 1963, when it was renamed the Stellite Division of the Union Carbide Company [1]. Research and development of new products was carried out in various locations during this time frame, as detailed in the following sections. A list of the wrought alloys developed during the Union Carbide years and which are still produced today is given in Table III along with the associated U.S. patent information and inventor names.

Table III. Wrought Alloys Developed from 1920 to 1969

Alloy	Inventor(s)	Location	U.S. Patent No.	Patent Issue /Other Date
B	Unknown	Long Island/ Niagara Falls	--	~1929[A]
MULTIMET	Russell Franks, William O. Binder	Niagara Falls	2,432,615	1947
W	Unknown	Niagara Falls	--	~1951[B]
25	William O. Binder	Niagara Falls	2,684,299	1954
X	Howard R. Spendelow, Jr., Walter Crafts	Niagara Falls	2,703,277	1955
N	Henry Inouye, William D. Manly, Thomas K Roche	Oak Ridge	2,921,850	1960[C]
C-276	See note[D]	--	--	1965-6[D]
188	Robert B. Herchenroeder	Kokomo	3,418,111	1968

[A] See text for more information.

[B] HASTELLOY W was developed specifically as a dissimilar weld metal and introduced around 1951. There is some evidence that it was developed with input from Rudy Thielman, then of Pratt & Whitney [3,4].

[C] During this time period, Oak Ridge National Laboratory was operated by Union Carbide. The first full-scale heats of INOR-8 (HASTELLOY N) were produced in Kokomo in 1957 [3].

[D] R. B. Leonard of Union Carbide Stellite Division (Kokomo) defined the final composition of HASTELLOY C-276 alloy, which was a low-carbon version of the alloy described by BASF in U.S. Patent No. 3,203,792 (licensed to Union Carbide), which itself was a low-silicon version of the original HASTELLOY C alloy [5].

Long Island/Niagara Falls Research Laboratories

Union Carbide had a research lab in Long Island, NY supporting Haynes Stellite Company until 1933, after that the research lab moved to Niagara Falls, NY [1]. Additionally, developmental work was performed at the Electro Metallurgical plant in Niagara Falls – also a part of Union Carbide. A number of new alloys and products were developed during this time period, including both cast and wrought alloys, as well as welding products. Possibly the most notable inventions of these early years were the HASTELLOY series of alloys. For some time, wrought forms of the company's alloys were melted in Kokomo or Niagara Falls, but sent outside for conversion forging, rolling, etc. In 1948, the company invested in the Wrought Alloy Plant to produce these product forms in-house. That mill facility, now known as the Deffenbaugh Street Operations (or DSO), is still in use today as the primary production facility for Haynes International.

The Original HASTELLOY Alloys The development of the original HASTELLOY series of alloys (A, B, C, and D) represented a major change for the company, providing new market areas beyond wear-resistant applications. The HASTELLOY alloys (trademark derived from "Haynes Stellite Alloy") provided excellent corrosion-resistance as well as high temperature strength. Credited for leading the development effort was Dr. Frederick M. Becket of Electro Metallurgical (and later V.P. of Haynes Stellite from 1923 to 1938) [1]. The first to be introduced was HASTELLOY A with a nominal composition of Ni-21Mo-19Fe-2Mn. The patent for this alloy (U.S. Patent No. 1,710,445) was issued in 1929, with Dr. Becket himself as the inventor. Applications for HASTELLOY A included those in the chemical process industry as well as high temperatures. One example of the latter was the hot wheel of a G.E.-built supercharger used in WWII [6]. The next alloy developed was HASTELLOY B (Ni-28Mo-5Fe-0.3V). While this alloy was developed by Union Carbide/Electro Metallurgical, no record could be found of the primary inventor. The high level of Mo in the new alloy resulted in high strength as well as corrosion-resistance, particularly to reducing acids. The composition of HASTELLOY B alloy was significantly different from an alloy (Ni-10Mo-10Fe) invented by Alvah W. Clement of the Cleveland Brass Manufacturing Co., but fell within the rather wide patent claims (U.S. Patent No. 1,375,083). The Clement patent was acquired by Union Carbide around 1930, just prior to the introduction of HASTELLOY B alloy [1,3]. While HASTELLOY B alloy found application in a vast array of corrosion-resistant applications, it was also used as a high-temperature alloy in applications such as forged supercharger blades, engine rings, and rocket nozzles on the Viking I and II Mars lander terminal descent systems.[6,7] Although HASTELLOY B has been replaced by the newer HASTELLOY B-3 alloy for use in reducing corrosion-resistant applications, it is still produced to this day for certain high-strength, high-temperature applications. The original HASTELLOY C alloy (Ni-16Cr-16Mo-5Fe-4W-0.7Si-0.5Mn-0.2V-0.06C) was patented in 1931 by Russell Franks (U.S. Patent No. 1,836,317). The addition of Cr was beneficial for both high temperature oxidation as well as oxidizing acid solutions. Since the Mo level was also relatively high, the resistance to reducing acids was also quite good. Originally introduced as a cast alloy, wrought processing techniques were soon developed. This alloy was put into service in both corrosion-resistant and high-temperature applications. High-temperature uses of HASTELLOY C alloy included the nozzle skirts on the F-1 engines which powered the Apollo Saturn V rocket, as well as the third-stage nozzle vane in Pratt & Whitney's J75 engine on the U-2 and other aircraft [3,8]. The modern-day C-family of alloys (C-276, C-4, C-22, C-2000, and C-22HS alloys) are used primarily in multi-purpose corrosion-resistant applications due to their strong resistance to both oxidizing and reducing acids. Modern high temperature applications for the C-family alloys are limited due to the superior oxidation resistance and thermal stability of more recently developed high temperature alloys. HASTELLOY D alloy (Ni-9Si-3Cu) was developed for sulfuric acid resistance and was used almost exclusively in cast form. The patent for this alloy was U.S. Patent No. 1,753,904 issued in 1930 to Clayton E. Plummer of Electro Metallurgical. The modern-day adaptation is HASTELLOY D-205 alloy, which is a wrought product known primarily for its resistance to sulfuric acid, particularly for very high concentrations. Due to their success in gas turbine applications, the early HASTELLOY alloys (particularly B and C) have been identified as the predecessors to the modern solid-solution strengthened superalloys [9].

MULTIMET alloy At the start of World War II, there was a pressing need for improved wrought high temperature alloys for gas turbine engines. Efforts to develop such alloys eventually led to the invention of MULTIMET alloy in 1945 [10]. (Note that another name for this alloy is N-155 alloy, which was the name used during the development of the alloy at the Niagara Falls Research Laboratory.) The key design properties of MULTIMET alloy (Fe-20Ni-20Co-21Cr-3Mo-2.5W-1.5Mn-1Nb-0.15N-0.12C) included good high temperature creep-rupture strength and oxidation resistance, as well as adequate fabricability and thermal stability. The composition could tolerate the large amount of Stellite and alloy S-816 scrap which was available in the post-war period [6,11]. At the time of the invention, MULTIMET had a unique combination of properties and was very effective in a large variety of gas turbine components, including tail-pipes and tail-cones, afterburner parts, exhaust manifolds, combustion chambers, turbine blades, buckets, and nozzles. One early example was the jet tail-cone and tail-pipe on the B-45, the first jet-powered bomber in the U.S. [10]. When the Wrought Alloy Plant was built in Kokomo in 1948, the highest volume alloy for several years was MULTIMET alloy [3]. Unfortunately, the lack of an in-house wrought processing facility during the initial development of the alloy led to unfavorable licensing agreements with competitors, and the full potential of the development was never fully realized. Indeed, this was one of the justifications which led to the construction of the new plant.

HAYNES 25 alloy During the debate in 1946 on whether or not to build the Wrought Alloy Plant in Kokomo, F. Sidney Badger (V.P. of R&D, 1944-1953) proposed a number of new products necessary for the success of the project [11]. First on this list was a readily fabricable high-temperature alloy. Work soon began and this was one of the main projects for the new high-temperature alloy development committee formed between Haynes Stellite and Niagara Falls. At a point well into the development of the new alloy, the U.S. Air Force (Wright Field) proposed specific requirements for a new sheet alloy for high-speed, jet-propelled aircraft [12-13]. Haynes Stellite declined the government funding since it was already far along on its own program, but agreed to develop the alloy to meet the Air Force requirements: 100h rupture lives at a load of 12 and 6 ksi (83 and 41 MPa) at 1700 and 1800°F (927 and 982°C), respectively. The result was called HAYNES 25 alloy (also known in the industry as L-605). Around the same time, a similar alloy was developed by Crucible Steel (which was funded by the Air Force). The alloys were similar enough that the two companies reached a cross-license agreement. HAYNES 25 alloy (Co-20Cr-15W-10Ni-1.5Mn-0.1C) had creep-rupture strength which far surpassed MULTIMET. In fact, until the recent advent of NS-163 alloy, HAYNES 25 alloy had the highest creep strength of the fabricable superalloys. Additionally, HAYNES 25 alloy is known for its excellent wear resistance, particularly against erosion and galling. Furthermore, HAYNES 25 alloy has excellent hot hardness and sulfidation-resistance. HAYNES 25 alloy has found application in numerous gas turbine components, including combustors, rings, seals, and blades. It has also been used in balls and bearings, forging dies, and a variety of industrial heating applications.

HASTELLOY X alloy The origin of HASTELLOY X alloy, one of the most widely used sheet alloys in the gas turbine industry, arose from post-war concerns about the supply of strategic elements (like Co, W, and Nb) in the possible event of a national emergency [11,14]. Both of the primary high-temperature sheet alloys of the time, MULTIMET alloy (Co,Nb,W) and HAYNES 25 (Co,W), contained significant quantities of these elements. The effort to develop a "low alloy content" alloy was successful, the result being HASTELLOY X alloy (Ni-22Cr-18Fe-9Mo-1.5Co-0.6W-0.1C), invented by Howard R. Spendelow, Jr. and Walter Crafts. The first commercial-scale heat was produced in Kokomo in 1951, and within 5 years the alloy was the biggest volume wrought alloy produced at the mill [3]. HASTELLOY X alloy has very good creep-rupture strength, especially considering its low alloy content and high Fe content. However, what really distinguished HASTELLOY X alloy over the other alloys of the time was its exceptional oxidation resistance. These features, combined with excellent fabricability, allowed HASTELLOY X alloy to be specified into a vast array of gas turbine applications, including combustors, transition ducts, spray bars, and flameholders, as well as numerous afterburner components. More than 60 years after its introduction, HASTELLOY X alloy remains one of the largest volume superalloys for gas turbine engines [15].

Technology Laboratories

In 1957, a new R&D laboratory facility was built on Park Avenue in Kokomo. It became the company's home for future alloy development work and remains in use to this day for the same purpose. The first two commercially successful developments, HAYNES 188 alloy and HASTELLOY C-276 alloy, were completed while the new Technology Labs were still under Union Carbide.

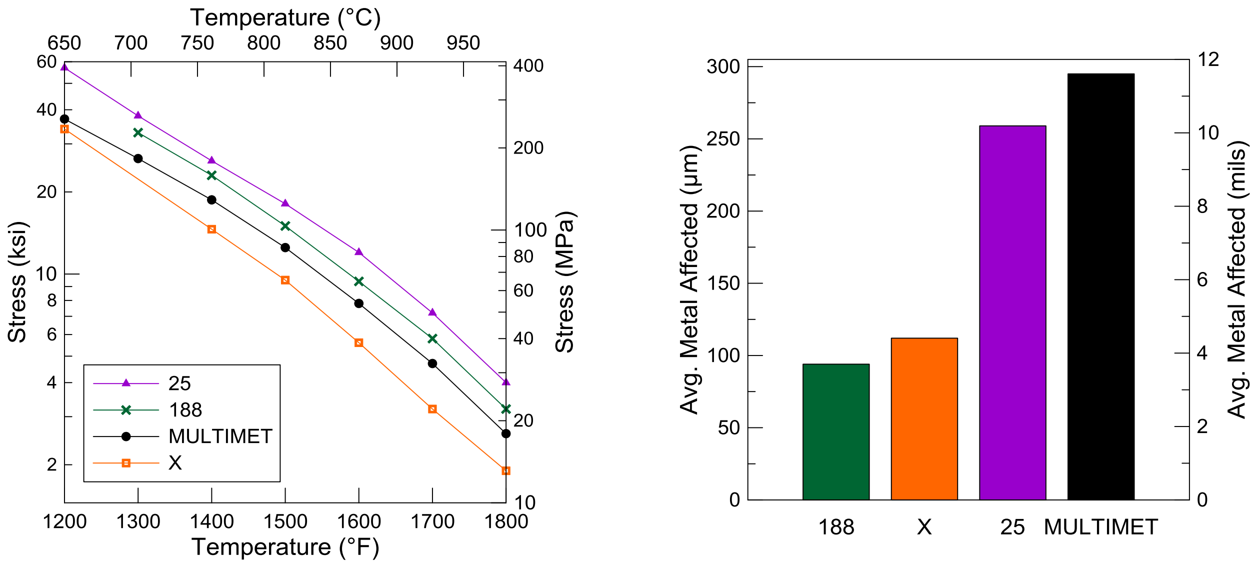

Figure 1. Comparative properties of 188 alloy vs. previously existing high-temperature alloys. a) 1000 hour rupture strength, b) oxidation resistance (1008 hour, 2000°F (1093°C), cycled weekly)

HAYNES 188 alloy The key features (see Figure 1) of HAYNES 188 alloy (Co-22Ni-22Cr-14W-1Mn-0.35Si0.1C-0.03La) are its high creep-rupture strength and oxidation resistance, the latter being significantly improved over previous Co-base alloys, such as HAYNES 25 alloy [16-17]. The alloy was also designed to have improved thermal stability over 25 alloy. 188 alloy was specifically tailored for critical, high-temperature sheet applications and has enjoyed tremendous success in a number of gas-turbine components, including combustor cans and liners, transition ducts, afterburner liners, turbine liners, nozzles, baffles, flameholders, and tail pipe liners. The matrix of 188 alloy has the fcc structure, which is stabilized due to the presence of Ni, Cr, Mn, and

C in sufficient quantity. Also present in the annealed condition are well-distributed M_6C carbides which serve to restrict grain growth during heat treatments and service exposures. Over long thermal exposures in the 1400 to 1600°F (760 to 871°C) range, some Laves phase can develop [16-17], but retained room temperature (RT) ductilities remain greater than 10%, even after 8000 hours [18]. The excellent oxidation resistance of the alloy has been associated with the addition of La (an element not found in HAYNES 25 alloy) as well its high Cr content. Being a Co-base alloy, 188 alloy also has excellent resistance to hot corrosion, sulfidation, and molten salt corrosion. HAYNES 188 alloy was invented by Robert B. Herchenroeder, who was inventor or co-inventor of four different alloys still produced by Haynes International and which have enjoyed commercial success.

Cabot Corporation Years (1970 to 1989)

In 1970, the Stellite Division was sold from Union Carbide to the Cabot Corporation. One of the strategies employed by the new management was to emphasize the production and supply of sheet products in both the aerospace and chemical process industries [15]. Renewed emphasis was put on alloy development, as well. A list of the alloys developed by the company during this time and still produced today is given in Table IV along with the inventor names and patent information.

Table IV. Wrought Alloys Developed from 1970 to 1989

Alloy	Inventor(s)	Location	U.S. Patent No.	Issue Date
C-4	F. Galen Hodge, Russell W. Kirchner William L. Silence	Kokomo	4,080,201	1978
S	Dennis S. Acuncius, Robert B. Herchenroeder, Russell W. Kirchner, William L. Silence	Kokomo	4,118,223	1978
556	Robert B. Herchenroeder, H. Joseph Klein	Kokomo	4,272,289	1981
G-30	Aziz I. Asphahani, William L. Silence, Paul E. Manning	Kokomo	4,410,489	1983
214	Robert B. Herchenroeder	Kokomo	4,460,542	1984
230	Dwaine L. Klarstrom	Kokomo	4,476,091	1984
C-22	Aziz I. Asphahani	Kokomo	4,533,414	1985
HR-160	George Y. Lai	Kokomo	4,711,763	1987

HASTELLOY S alloy The project to develop HASTELLOY S alloy began from a request from Pratt & Whitney for an improved low thermal expansion alloy [19]. The properties requested were: 1) thermal expansion exhibited by HASTELLOY B alloy, 2) tensile strength of HASTELLOY X alloy, 3) oxidation resistance of HASTELLOY X alloy, and 4) formability of HASTELLOY N alloy. Furthermore, the alloy should have improved thermal stability compared to the other high temperature alloys of its day. This was a very difficult request to fulfill due to the opposing effects of the key alloying elements on the critical properties. The target for the thermal expansion requirement was soon relaxed to restrict the mean coefficient of thermal expansion from RT to 1800°F (982°C) to below 8.7×10^{-6} in/in/°F (15.7×10^{-6} m/m/°C). A systematic study was performed in short order and production material was produced within only 13 months (see Figure 2). The invention of the new HASTELLOY S alloy (Ni-16Cr-15Mo-0.5Mn-0.4Si-0.02La) was led by Dennis S. Acuncius who attributed the low thermal expansion to the proper balance of the nickel, chromium, and molybdenum contents and the excellent oxidation resistance to small, but effective additions of Si, Mn, and La [20]. The alloy was specified into a number of components including seal rings in particular, which required low thermal expansion for thermal fatigue resistance as well as dimensional control. Other early applications included burner cans and engine casings.

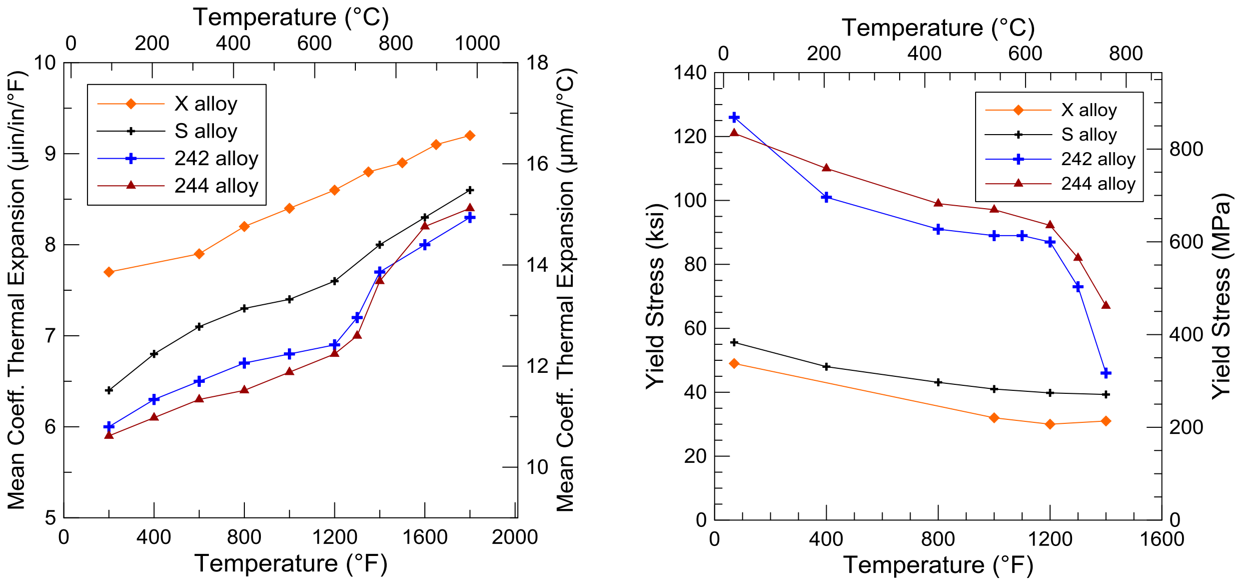

Figure 2. Comparative properties of low thermal expansion alloys. a) Coefficient of thermal expansion, b) Yield strength.

HAYNES 556 alloy This alloy was designed as a major improvement over MULTIMET alloy. While MULTIMET alloy had been successful, its biggest drawback was its average oxidation resistance. The objective behind the design of 556 alloy (Fe-20Ni-18Co-22Cr-3Mo-2.5W-1Mn-0.4Si-0.6Ta-0.2Al-0.2N-0.1C-0.02Zr-0.02La) was to produce an alloy with similar high temperature strength as MULTIMET alloy, but with better oxidation resistance. This goal was achieved through careful control of several minor elements [21]. The Nb present in MULTIMET alloy was replaced by Ta in the new 556 alloy. Niobium was found to be detrimental to oxidation, while the Ta additions did not have an adverse effect, and in fact may have been beneficial. More importantly, La was added to the alloy for improved scale adhesion. Al and Si were also carefully controlled to improve oxidation resistance. The end result was an alloy with significantly better oxidation resistance than MULTIMET alloy. The new 556 alloy also had improved weldability over MULTIMET alloy, particularly regarding heat affected zone (HAZ) cracking. This was attributed, in part, to the La addition [21]. However, it has also been shown that the substitution of Ta for Nb also played a role in the weldability improvement [22]. While 556 alloy was designed for aerospace applications (high strength, oxidation resistance, and fabricability), it has found a number of applications where resistance to corrosive, high-temperature environments is required. These have included waste incinerators, rotary calciners, and industrial gas turbines burning low-grade fuels. Many of these environments are sulfur-bearing and are thus well-suited for 556 alloy (low Ni, high Co and Fe).

HAYNES 214 alloy The vast majority of wrought high temperature alloys derive their oxidation resistance from the formation of a protective chromia surface oxide layer. While often this provides adequate protection, sometimes surface coatings are applied for additional oxidation-resistance. These include the NiCrAlY-type coatings, so-called due to their compositional make-up. These coatings protect through the formation of an alumina surface oxide layer which is considerably more protective than chromia. The novel concept behind HAYNES 214 alloy (Ni-16Cr-4.5Al-3Fe-0.04C-0.01Y) was to make a wrought, fabricable alloy which could take advantage of this type of oxidation-resistance [23]. To turn this concept into reality, it was necessary to lower the amount of Y, since it was found to result in grain boundary oxidation and incipient melting when present in too high a concentration (the latter issue resulting in problems with cracking during hot working as well as during welding). Another important aspect of this invention was to limit the amount of the gamma-prime phase by limiting the amount of Al to around 4.5 wt.%, as well as the inclusion of around 3 wt.% Fe which lowers the gamma-prime solvus and reduces its embrittling characteristics. The result of the development program was a success, and HAYNES 214 alloy is well-known as the most oxidation-resistant alloy available as a conventionally produced sheet product. The alloy can indeed be fabricated and welded, but it is necessary to take precautions to alleviate potential effects of gamma-prime formation. The modest strength of the alloy at very high temperatures (generally where oxidation-resistance is the most needed) does limit it to applications where strength is not as important. Gas turbine applications for 214 alloy include honeycomb seals and combustor splash plates. In other industries, 214 alloy has been used in burner assemblies, furnace hardware (including mesh belts), refractory anchors, and fume hoods.

HAYNES 230 alloy In the 1970's, the "cobalt crisis" led to multiple efforts to develop alloys with reduced Co levels. One such effort resulted in the invention of HAYNES 230 alloy (Ni-22Cr-14W-2Mo-0.5Mn-0.4Si-0.1C-0.02La) [24-26], perhaps the premier solid-solution strengthened alloy currently available today. The success of the invention by Dr. Dwaine L. Klarstrom went beyond achieving the basic goal to develop an alloy with excellent high-temperature strength while having no Co requirement. The new alloy also possessed significantly improved thermal stability compared to alloys such as 188 alloy and HASTELLOY X alloy. Remarkably, 230 alloy has been demonstrated to be free of deleterious phases even after 50,000 hours of thermal exposure [27]. Moreover, the oxidation resistance of the new 230 alloy was superb, surpassing or equaling all other chromia-formers in its alloy class [28-29]. The alloy is resistant to grain growth at even very high temperatures, as evidenced by its very high annealing temperature, 2250°F (1230°C). Even with such a high annealing temperature, 230 alloy has a relatively fine grain size which has beneficial effects on its low cycle fatigue (LCF) resistance [30]. With this impressive combination of properties, 230 alloy has found application in numerous gas turbine components such as combustors, transition ducts, flameholders, nozzles, injectors, and thermocouple sheaths. Other applications have included high temperature heat exchangers, furnace retorts, recuperator internals, heat treating hardware, burner components, nitric acid support grids, and many more.

Haynes International (1989 to 2000)

Haynes International became an independent company for the first time since 1920 when the sale of Cabot Corporation's Kokomo-based wrought products component was completed in 1989. The wear technology component, including the Stellite trademark, had been sold separately. Fortunately, the R&D facilities in Kokomo remained intact as part of Haynes International's corporate headquarters complex. Several new and ongoing alloy developments were completed during the first few years of the new corporate structure. A list of the alloys developed by the company during this time is given in Table V along with the inventor names and patent information.

Table V. Wrought Alloys Developed from 1989 to 2000

Alloy	Inventor(s)	Location	U.S. Patent No.	Issue Date
242	Michael F. Rothman, Hani M. Tawancy	Kokomo	4,818,486	1989
HR-120	Michael F. Rothman, Dwaine L. Klarstrom, George Y. Lai	Kokomo	4,853,185 4,981,647	1989 1991
ULTIMET	Paul Crook, Aziz I. Asphahani, Steven J. Matthews	Kokomo	5,002,731	1991
D-205	Narasi Sridhar	Kokomo	5,063,023	1991
C-2000	Paul Crook	Kokomo	6,280,540	2001*
B-3	Dwaine L. Klarstrom	Kokomo	6,503,345 6,610,119	2003* 2003*

*While the C-2000 and B-3 alloy patents were issued after 2000, they were commercially introduced in the 1990's.

HAYNES 242 alloy One of the more interesting alloys invented by Haynes International was 242 alloy. This low-thermal expansion alloy was the first alloy designed to be intentionally strengthened through heat treatment by the $Ni_2(Mo,Cr)$ phase [31-33]. This phase had been previously been observed in several Ni-Cr-Mo alloys (C-276, S, and C-4 alloys) after long term thermal exposures, but prior to 242 alloy had not been utilized for intentional strengthening due to the lengthy aging treatments required to form. The composition of 242 alloy (Ni-25Mo-8Cr) was selected to allow for full hardening within 48 hours. The vast majority of age-hardenable nickel-base alloys are strengthened by the gamma-prime phase, which is an effective strengthener, but can be susceptible to overaging, reduce ductility, and can lead to difficulties in fabrication and welding. In contrast, the $Ni_2(Mo,Cr)$ precipitates (often referred to as long range ordered (LRO) domains) in 242 alloy do not overage, do not significantly lower ductility, and are sluggish to form, thus allowing sufficient time for heating and cooling operations during the manufacture of components to occur without strengthening. The result is a very strong, ductile, fabricable, and weldable alloy. Moreover, the alloy has enough Cr to provide sufficient oxidation resistance so that that it can be placed into service without a coating. As a result of these properties, combined with a low coefficient of thermal expansion, 242 alloy has been used frequently as a seal ring material in gas turbine engines. The success of 242 alloy has led to a new family of $Ni_2(Mo,Cr)$-strengthened alloys which includes the recent C-22HS and 244 alloys.

HAYNES HR-120 alloy The HAYNES HR-120 alloy was developed as a significant improvement (in terms of creep strength) over austenitic Fe-Ni-Cr and Ni-Cr-Fe type alloys, such as 800H and 600, respectively. HR-120 alloy (Fe-37Ni-25Cr-0.7Nb-0.7Mn-0.6Si-0.2N-0.05C) achieves its excellent creep strength from the formation of effective niobium-rich and chromium-rich nitrides and carbonitrides [34]. The high Cr level also provides very good oxidation resistance. Figure 3 provides comparative rupture strength and oxidation resistance data for HR-120 vs. several solid-solution strengthened superalloys. Additional characteristics of HR-120 alloy include good resistance to sulfidizing, carburizing, and hot corrosion environments. Applications in the gas turbine industry include the shrouds, struts, and stators for large frame industrial turbines and in microturbine recuperators. The alloy has also been used in a variety of industrial heating components, such as heat treat baskets, retorts, mesh belts, and hinge pins.

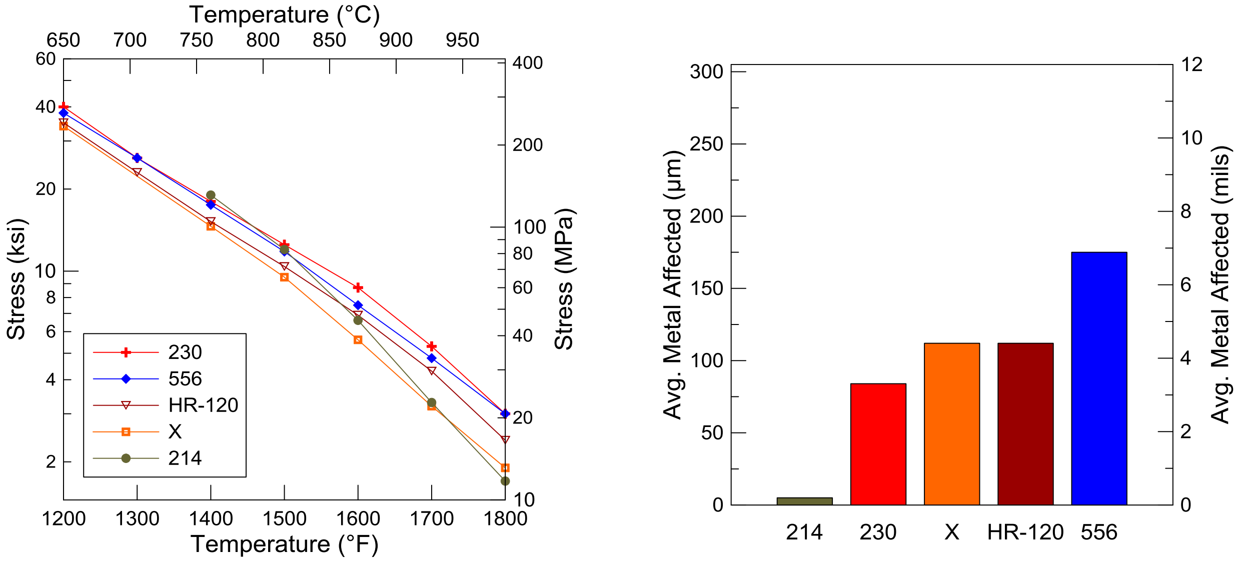

Figure 3. Comparative properties of several modern solid-solution strengthened superalloys. a) 1000 hour rupture strength, b) oxidation resistance (1008 hour, 2000°F (1093°C), cycled weekly)

Haynes International, 21st Century (2001 to Present)

After the invention of the HASTELLOY B-3 and C-2000 alloys (patents for both submitted in 1994), there followed a period of significantly limited alloy development activity with no new patent application filings for a period of 8 years. The revival of the alloy development activities in the late 1990's was overseen by Michael F. Rothman, V.P. of Engineering and Technology from 1995 to 2005. Subsequently, over the last 12 years Haynes International introduced 8 new alloys, both high-temperature and corrosion-resistant. A list of the first 7 of these alloys is given in Table VI along with the inventor names and patent information. The latest alloy, the metal dusting and corrosion resistant HAYNES HR-235 alloy, was introduced in 2013.

Table VI. Wrought Alloys Developed from 2001 to Present

Alloy	Inventor(s)	Location	U.S. Patent No.	Issue Date
G-35	Paul Crook	Kokomo	6,740,291	2004
C-22HS	Lee M. Pike	Kokomo	6,860,948	2005
HYBRID-BC1	Paul Crook	Kokomo	7,785,532	2010
282	Lee M. Pike	Kokomo	8,066,938	2011
NS-163	S. Krishna Srivastava	Kokomo	8,075,839	2011
HR-224	Dwaine L. Klarstrom, Steven J. Matthews, V. R. Ishwar	Kokomo	8,506,883	2013
244	Lee M. Pike, S. Krishna Srivastava	Kokomo	8,545,643	2013

<u>HAYNES 282 alloy</u> The driving force for the development of 282 alloy was the need for a gamma-prime strengthened superalloy with both excellent creep strength and fabricability. Additionally, it was desired that the alloy should have good thermal stability. The currently existing gamma-prime strengthened superalloys suffered from either relatively low creep strength (263 alloy) or limited fabricability (Waspaloy and R-41 alloy). It was discovered that by controlling the gamma-prime content to an intermediate level, a balance between strength and fabricability could be achieved [35-36]. Furthermore, to achieve the requisite creep-rupture strength (and maintain good thermal stability) it was further necessary to carefully control the solid-solution strengthening element, Mo. The result was HAYNES 282 alloy (Ni-20Cr-10Co-8.5Mo-2.1Ti-1.5Al-0.06C), which has creep strength surpassing Waspaloy alloy and approaching R-41 alloy, despite having considerably lower gamma-prime content than either of these alloys (see Figure 4a). Not surprisingly, the creep strength of 282 alloy is also superior to the lower gamma-prime content 263 alloy. The superior weldability of 282 alloy is illustrated in Figure 4b, where the results of the controlled heating rate tensile (CHRT) test are provided. The CHRT test, an adaptation by Haynes [37] of a test first designed by Rocketdyne [38], measures as-annealed, intermediate temperature elongation as an indicator of resistance to strain age cracking, a problem often associated with gamma-prime containing alloys. As shown, 282 alloy has considerably higher elongation than either Waspaloy alloy or R-41 alloy, indicating its greater resistance to strain-age cracking. Since its introduction, reported customer experiences with welding 282 alloy have been overwhelmingly positive and the alloy has been successfully welded into several different configurations, included dissimilar alloy combinations. Applications for 282 alloy include turbine cases, transition ducts, combustors, and others.

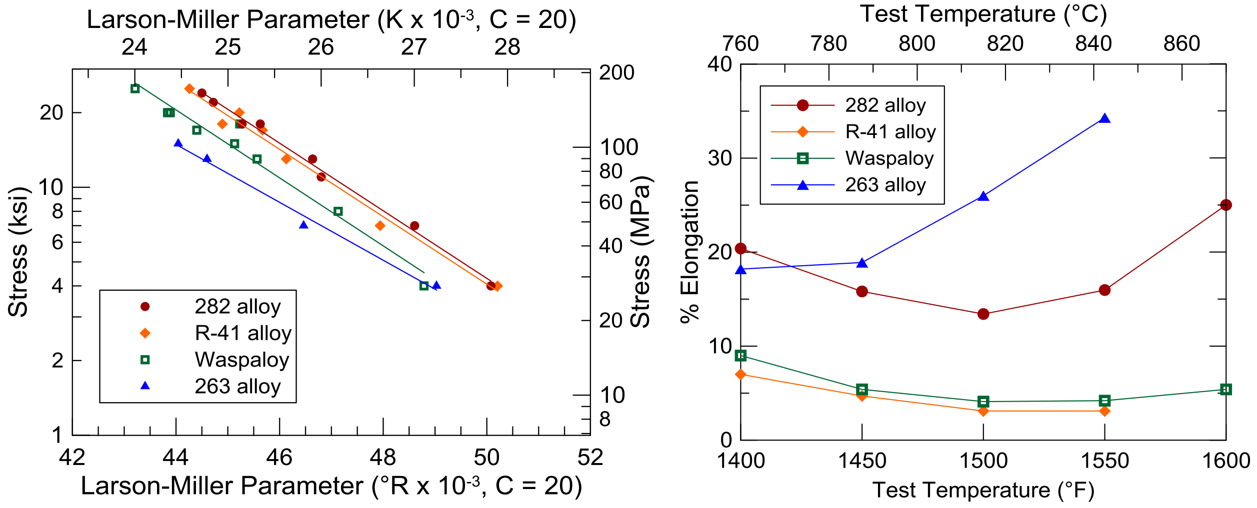

Figure 4. Comparative properties of 282 alloy vs. other fabricable gamma-prime strengthened superalloys. a) 1% Creep strength, b) CHRT test (resistance to strain-age cracking).

<u>HAYNES NS-163 alloy</u> Advances in fabricable superalloys, particularly those produced in sheet form, have primarily focused on properties other than creep-rupture strength, for example, oxidation, fabricability, and strategic element content. For decades, HAYNES 25 alloy was the fabricable sheet alloy with the greatest creep-rupture strength. While the ODS alloys did possess both excellent creep strength and oxidation resistance, they were certainly not “readily” fabricable - a direct result of the presence of the strengthening oxide dispersions. The concept behind NS-163 alloy (Co-28Cr-21Fe-8Ni-1.3Ti-1Nb-0.1C) was to create an alloy which could be produced into a component in a conventional manner (ingot metallurgy, hot/cold working, cold forming, and/or welding) prior to being imparted with excellent strength [39]. The final step in fabrication

of an NS-163 component would be a gas nitriding heat treatment which results in a thru-thickness dispersion of strengthening Ti- and Nb-rich nitrides (see Figure 5a). Due to the nature of this process, it is restricted to product forms with a relatively small cross-section, such as sheet, wire, and powder. After nitriding, the creep-rupture strength of the alloy far surpasses any other fabricable superalloy (see Figure 5b). The stability of the nitrides maintains the excellent creep-rupture strength of the alloy to temperatures as high as 2200°F (1204°C). The alloy is a candidate for a number of gas turbine components which could be made from sheet, and its high creep-strength may allow for gas turbines to be operated at temperatures previously not achievable.

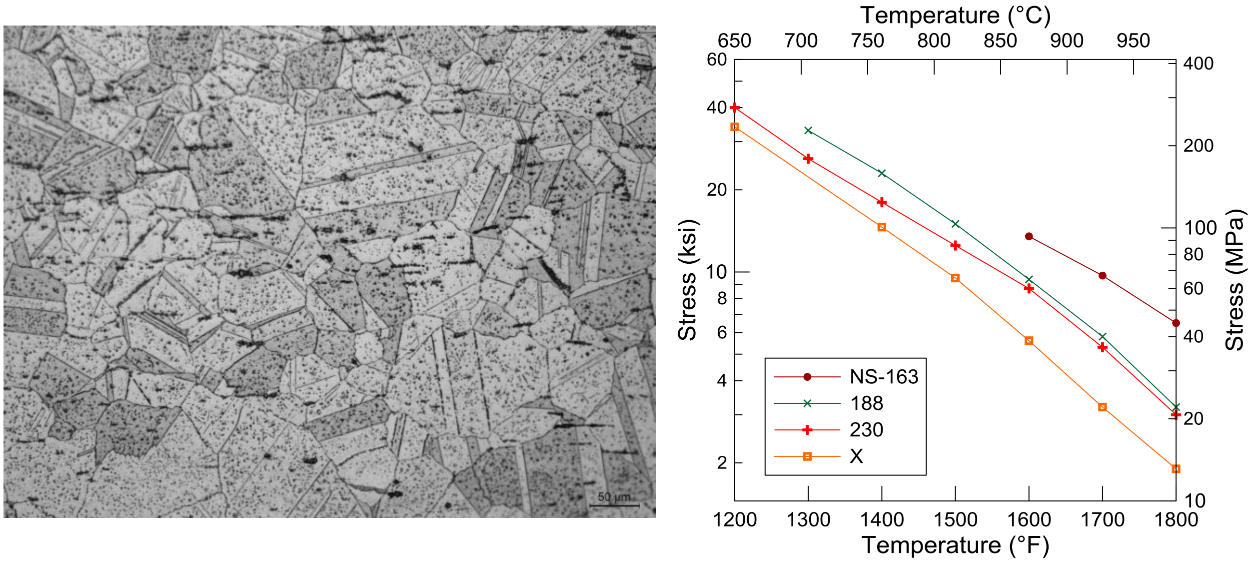

Figure 5. a) Typical optical micrograph of NS-163 alloy in the as-nitrided condition, b) Comparative 1000 hour rupture strength.

<u>HAYNES HR-224 alloy</u> The recently introduced HR-224 alloy was designed to address one of the limitations of 214 alloy – its fabricability. While it is certainly possible to fabricate components out of 214 alloy, the precipitation of relatively large amounts of the gamma-prime phase can make it challenging. To alleviate this issue, HR-224 alloy (Ni-27.5Fe-20Cr-3.6Al-0.3Ti-0.3Si-0.05C) was developed with a lower Al content and a greater Fe content than 214 alloy. The result is a much more fabricable alloy with the same excellent oxidation resistance. The oxidation behavior has been recorded in several oxidizing environments, including flowing air, water vapor, and combustion gases at temperatures ranging from 1400 to 1800°F (760 to 982°C) [40]. In all cases the formation of the protective alumina layer provided excellent oxidation resistance. Recent data suggests the alloy maintains excellent oxidation at temperatures as high as 2200°F (1204°C). However, at such high temperatures the alloy may be limited to non-load bearing applications due to its relatively low creep strength at temperatures above the gamma-prime solvus. Potential applications for the alloy include microturbine recuperators, heat exchangers, catalytic converters, strand annealing tubes, and heat shields.

<u>HAYNES 244 alloy</u> The latest patented alloy developed by Haynes International is 244 alloy (Ni-22.5Mo-8Cr-6W), commercially introduced in 2012 [41]. The new low thermal expansion alloy provides a significantly increased upper service temperature compared to 242 alloy. The invention was based on the discovery that partial W substitutions for Mo partition to the LRO domains and increase the order-disorder temperature to greater than 1400°F (760°C) [42]. As a result, the yield strength (Figure 2b), creep-rupture strength, and LCF resistance of 244 alloy at 1400°F (760°C) are much superior to 242 alloy. The Ni_2(Mo,Cr,W) domains do not appear to be susceptible to

overaging, with the high temperature strength of the alloy being retained even after 8,000 hours at 1400ºF (760ºC). Another benefit of W is that it is more effective than Mo in lowering the coefficient of thermal expansion (see Figure 2a). The new alloy is being considered for gas turbine applications, including turbine cases and seal rings in engines where operating temperatures are being raised beyond current capabilities.

Future Alloy Development

Haynes International has a storied history, spanning over a century, of invention and development of new alloys to meet ever changing and increasingly demanding materials requirements. The company remains committed to the relentless pursuit of these challenges. Recent investments in the Research and Technology (R&T) department, including both laboratory equipment and technical personnel, have positioned the company well to continue its tradition of innovation well into the 21st century.

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