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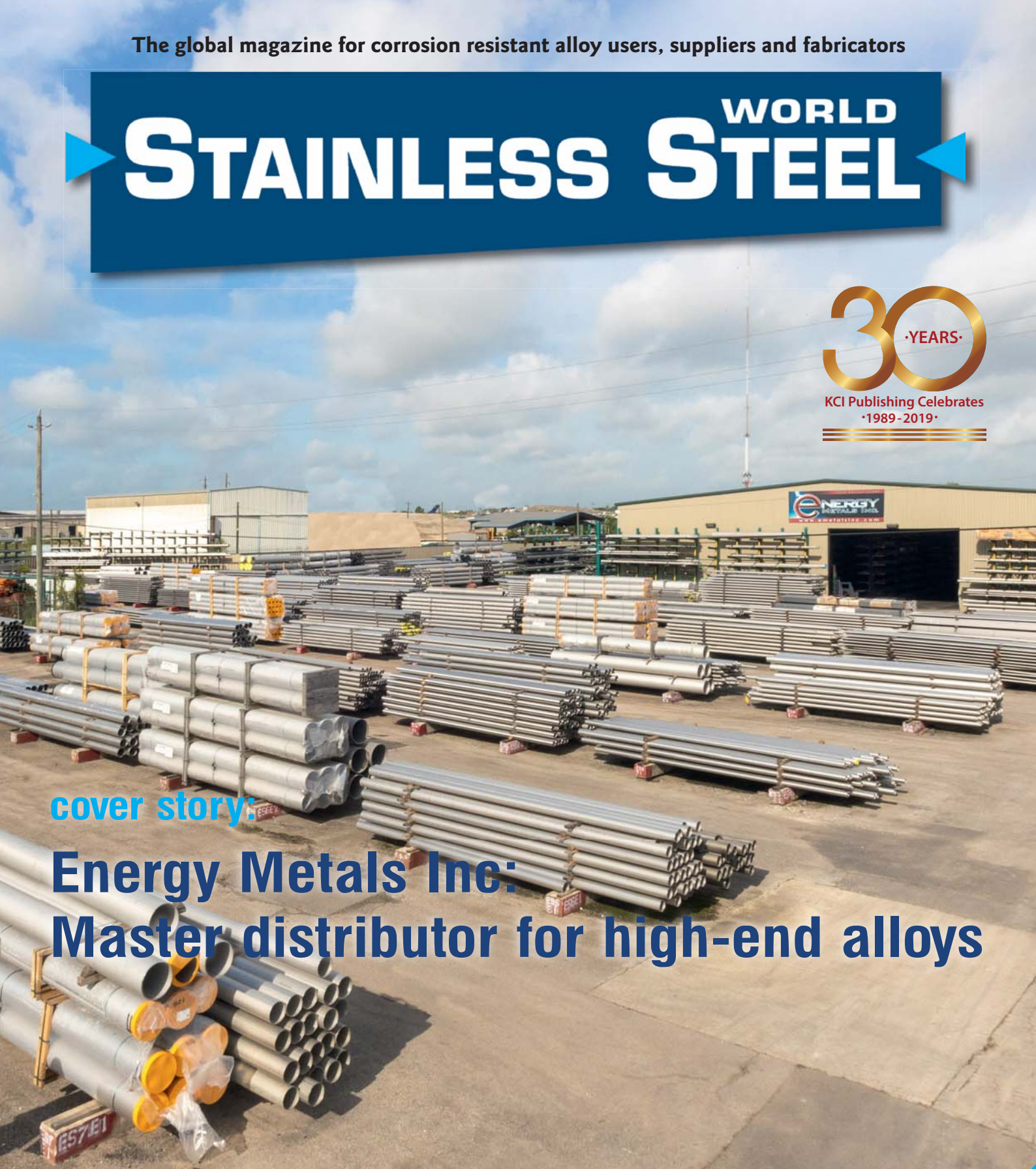

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Ferralium 255 – The original super duplex stainless steel

Considered to be the very first super duplex stainless steel on the market, Ferralium® 255 was launched in 1969. After 50 years of successful application and continuous development, the history of this unique alloy is shared in further detail.

By Rodney Rice

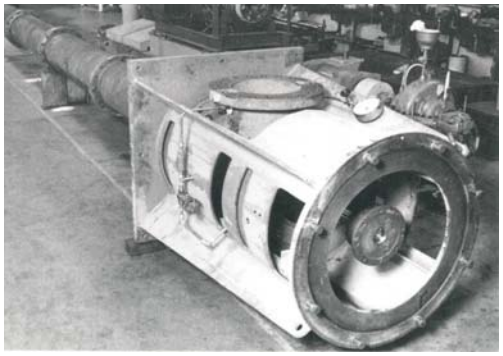
The initial patent

The origins of Ferralium as the first super duplex stainless steel (SDSS) can be dated back to a patent application made by Langley Alloys in 1967. Given the somewhat non-descript title "Improvement in Stainless Steels" it described the issues facing this family of alloys at that time, together with the answer to these issues. Austenitic stainless steels were well accepted in the market, with good corrosion resistance inferred by their relatively high chromium and nickel content. However, their tensile properties were generally low. In comparison, various martensitic (precipitation hardening) grades could achieve much higher strengths through heat treatment, but with lesser corrosion resistance.

Rather than seeing a mixed austenitic/ferritic microstructure as a problem, the patent turned that feature into a virtue. Changes in steelmaking practice allowed the controlled addition of nitrogen, balanced by a precisely defined composition, and optimised by careful processing and heat treatment.

The role of nitrogen in super duplex stainless steels

Nitrogen has been present in steel as long as steel-making has taken place. This content had been unintentional and, for many years there was no means of removing or controlling the nitrogen concentration. Modern steelmaking techniques such as AOD and VOD that were implemented from the 1970's onwards allowed much cleaner steels to be produced and nitrogen to be removed. However, before that breakthrough, Langley Alloys were able to increase nitrogen levels by using nitrogen-enriched ferrochrome briquettes to push the nitrogen level up towards 0.40% from the ambient level of 0.06%.



The development of North Sea oil in the UK led to a surge in the requirements for newer alloys with greater levels of performance. Here are components for line shaft pumps specified in Ferralium as an alternative to Alloy K-500.

The presence of nitrogen in duplex microstructures has multiple benefits.

1. It increases the yield strength and contributes to Ferralium being the only SDSS that achieves a yield strength > 85ksi (586N/mm2) compared with 80ksi (550N/mm2) for regular grades.
2. It positively improves pitting corrosion resistance. The PREN (pitting resistance equivalent number) formula utilises a factor of 16 for the nitrogen content, compared with 3.3 for the molybdenum content and 1 for the chromium content. Ferralium has a PREN > 40 and therefore provides excellent corrosion resistance in many aggressive environments.
3. It also contributes to the formation of an ideal microstructure. Nitrogen is an austenite stabiliser, helping to achieve a balance between austenite and ferrite, thereby combining the favourable properties of both (higher strength, resistance to stress corrosion cracking, excellent erosion/corrosion resistance).

The benefit of copper

Copper has been a fundamental element to mankind for many thousands of years, with widespread use in construction, piping and cooking utensils. Along with excellent thermal (and electrical) conductivity, it resists corrosion and fouling. As an addition to Ferralium it significantly increases pitting corrosion resistance. It is believed to heighten the passivating properties of molybdenum and reacts with absorbed sulphides on the surface, forming an insoluble copper sulphide 'protective layer' that stifles ongoing corrosion that occurs near inclusions and other breaks in the passive film of this stainless steel. As such, it helps to achieve superior resistance in seawater and many acids such as sulphuric, nitric and phosphoric acids.

The benefit of copper is recognised elsewhere. For instance, Hastelloy® C2000 stands apart from other nickel alloys for its deliberate addition of copper to enhance resistance to sulphuric acid. Despite this recognition, Ferralium remains unique amongst stainless steels for its high level of copper addition, contributing to its superior performance; it contains almost 2.0% copper, whereas S32750 contains no more than 0.5% copper and S32760 no more than 1.0% copper.

Rather unusually, Ferralium was used during the refurbishment of the Statue of Liberty. As previously written about in Stainless Steel World, it was used to replace corroded sections of the inner structure.

Welding practices

In the early years of their development, particularly in plate form, concerns around weldability were often sufficient to prevent the adoption of SDSS despite the excellent cost/performance advantage. Retaining the favourable duplex microstructure can be problematical when welding, as high heat input can result in more ferrite than austenite in the weld zone, together with the formation of deleterious phases such as σ and brittle intermetallic phases. This can result in a significant loss of impact strength, and more significantly corrosion resistance, in this region resulting in rapid failure.

Through a more complete understanding of these metallurgical phenomena, Langley Alloys was able to demonstrate that SDSS can be welded to achieve excellent properties. Well qualified weld procedures, controlled heat input and inter-pass welding temperatures, using over-alloyed filler metals and appropriate shield gases can all contribute to robust joins.

Nickel price volatility

The uptake of SDSS was given some help from an expected source – nickel prices. As an expensive addition to stainless steels and other high-performance alloys, its price can influence the relative competitiveness of different grades. SDSS contains 5% nickel, but this is typically less than half that of regular austenitic grades (i.e Alloy 316L – 10%), less than a quarter of that of super austenitic grades (i.e. Alloy 254 -18%) and less than a tenth of that of common nickel alloys (i.e. Alloy 625 -58%). Following the original development of Ferralium 255, the price of nickel rose steadily, and in 1979 it became the 7th metal to be listed on the London Metal Exchange. Although this gave some transparency in global pricing, it could not prevent a huge price spike in the late 1980's. This was caused by a reduction in mining capacity as producers responded to a sluggish market, together with an uptick in production of stainless steels across Europe and the USA. It took around four years for the market to correct itself. Throughout this period there was an obvious benefit arising from the substitution of both nickel and super austenitic alloys by SDSS. Even now, the greater volatility of nickel prices can benefit the specification of SDSS as prices are more stable between quotation and delivery.

During the 1980's, the addition of flue gas scrubbers to reduce emissions from fossil fuel burning power stations was a perfect application for Ferralium due to its high levels of corrosion resistance to the fluids used.

The value of marketing

Ferralium is one of several trademarks registered by Langley Alloys. It was originally registered in 1958, and first

utilised in 1969 when the developmental 'Langalloy 40V' product was branded, as soon as the patent covering its development was granted.
Competing super duplex alloys were subsequently developed and a similar trademarking approach adopted:

- Mather & Platt patented what became known as Zeron 100 some years later in 1982. Ownership of the Zeron® trademark has subsequently moved from Mather & Platt to Weir Materials to Rolled Alloys. Once the original patent matured it was possible for other manufacturers to produce their version of UNS32760.
- Similarly, Sandvik Materials Technology sought to trademark their original version of what is now most commonly recognised as UNS S32750, as Sandvik SAF2507® in 1987.

Langley Alloys has promoted a variety of product forms under this trademark. For instance, cast and forged specifications were developed, alongside a specification for fasteners, another for valve body castings and so on. A range of complementary products such as weld wire as well as various guidelines for machining, etc. helped to support the new alloy. Those early specifications still hold, as many years after items originally entered service we are contacted to help source replacements.

Ferralium was used to encapsulate waste nuclear waste for storage. The image shows one of the SDSS containers being impacted tested.

The Haynes years

Haynes International is perhaps best known for the development of innovative high-temperature alloys such as the Hastelloy® range. However, it is less well-known that throughout the 1970's and 1980's they actually produced Ferralium 255 under licence from Langley Alloys. Primarily supplied as rolled bar and plate, it has been widely used across the chemical process industry due to its superior resistance to many acids. During this time, Haynes supplied Ferralium 255 bars for the refurbishment of the Statue of Liberty statue.
Although Haynes no longer produce Ferralium 255, the work they undertook in promoting the virtues of this unique alloy still persist. Langley Alloys facility near Portland, Oregon specialises in the processing and distribution of SDSS plate. They were previously an independent distributor, operating as National Metal Distributors, as a customer of both Haynes and Langley Alloys, before acquisition by Langley Alloys in 2010.

Changes at Langley Alloys

In the 1960's Langley Alloys was a very different business to that of today. From its early roots in the development of copper alloys for naval and aerospace applications in the 1930s, it still operated a foundry, forge and rolling mills. In fact, it also produced a range of industrial valves that utilised the SDSS alloy developments. Following the relocation of the business in the 1980s, and subsequent divestment of the foundry, today's business emerged in the late 2000s as a focused distributor of high-performance alloys. However, it still retains ownership of the trademarks, patents and the technical know-how that sits behind Ferralium and several other unique alloys. A programme of R&D is still ongoing to extend the benefits of this alloy into the next 50 years.

Ferralium is widely specified in components for fertiliser and urea manufacture. Here are parts recently fabricated in plate, for sections where continued exposure to phosphoric acid and abrasive solutions poses a significant challenge to alloy selection.