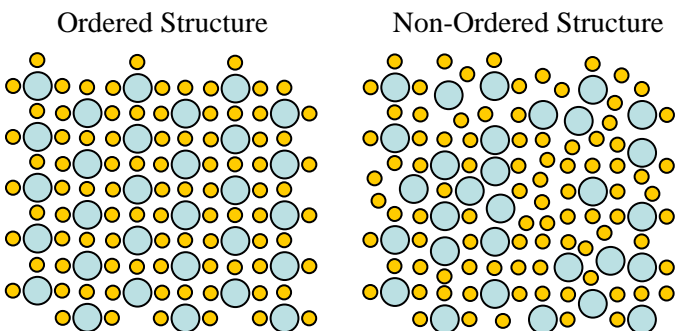




INTERMETALLIC MATERIALS are a unique class of materials having characteristics of both metals and ceramics. They differ from conventional metal alloys in that they generally possess long-range-ordered crystal structures. The predominant bonding patterns found in ceramics are highly directional covalent and ionic bonds, whereas the unique deformation properties of metals are due to non-directional metallic bonding. Intermetallics contain both metallic and covalent bonds, depending on the constituent metals. Mixed bonding provides mechanical properties that are



between metals (which are generally softer and more ductile) and ceramics (which are generally harder and more brittle).

High-temperature strength and superior oxidation resistance make intermetallic materials exceptional candidates for use in high temperature component design providing not only longer equipment service-life but the potential to operate at above normal temperatures. Promising applications include heat-treating fixtures, transfer rolls for hot metal processing, forging dies, radiant burner tubes, or pyrolyzer parts. The high-temperature strength and superior oxidation resistance of these materials would allow increases in operating temperature for many industrial processes, with resulting dramatic improvements in thermal energy efficiency and reduced residence time of chemical reactants at critical temperatures.

INTERMETALLIC DEVELOPMENT

The Department of Energy (DOE) began funding the investigation of intermetallic materials at the Oak Ridge National Laboratory (ORNL) in 1981.¹ It has been one of the longest continuously funded materials development programs ever undertaken. Initial work focused on basic investigations of the effects of microstructure, identification of alloying elements, and the development of thermochemical and thermomechanical property databases.

The DOE Office of Energy Efficiency and Renewable Energy's Industrial Technologies Program (ITP) recognized that the unique properties of intermetallic compounds could enable the development of new, energy-efficient technologies and process systems. ITP began funding R&D on nickel aluminide intermetallics in the early 1990s. As a result of cost-shared R&D with industrial partners, intermetallic alloys have been deployed commercially in a variety of manufacturing applications.

NICKEL ALUMINIDE INTERMETALLICS

ORNL identified the nickel aluminide intermetallic (Ni_3Al) as having unique high-temperature strength and oxidation resistance. Its highly ordered crystal structure provides increased creep and yield strengths with peak yield strength approximately 30 to 40% higher at 1475 to 1650°F (800 to 900°C) than at room temperature. Since nickel aluminide alloys contain up to 12 wt % excess aluminum, they form a protective aluminum oxide (Al_2O_3) coating which slows oxidation. This results in exceptional resistance to carburization and coking at high temperatures – a characteristic making it ideal for use in heat treating furnaces, steelmaking, and other manufacturing processes.

BARRIERS TO USE

Despite the useful properties inherent to the Ni_3Al structure, the brittle texture of the material long limited its usefulness in industrial settings. Industrial materials need to be able to absorb and respond to sudden pressure changes and mechanical impacts without catastrophic failures typical of ceramic or brittle materials. In addition, an intermetallic's unique structural benefits can be lost when using traditional metal fabrication techniques, particularly forming and welding. The commercial application of Ni_3Al to industrial processes required the development of Ni_3Al alloys with reduced brittleness and an increased capability for shape casting, forming and welding into useful structures.

PATHWAY TO SUCCESSFUL COMMERCIALIZATION

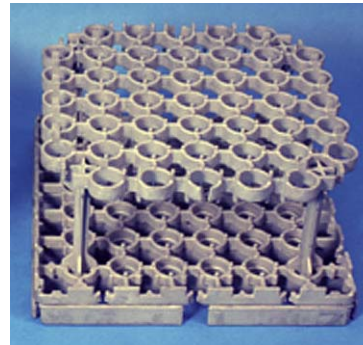
By adding boron and controlling the nickel-to-aluminum ratio, ORNL scientists were able to develop Ni_3Al alloys exhibiting ductility at room temperature. Further chemistry modifications improved intermediate-temperature ductility and high-temperature oxidation resulting in compositions that were potentially useful for industrial applications.

Controlled composition ductile alloys were difficult to make, and commercialization was hindered until the early 1990s when ORNL developed a process suitable for producing industrial quantities of the intermetallic materials. The “Exo-Melt™” process uses a specialized furnace-loading arrangement to control the exothermic heat from the reaction of aluminum with nickel; energy is provided more rapidly to the materials while the ideal composition concentrations are maintained. This process reduces melting and holding times and minimizes silicon pick-up and other reactions with furnace refractories. Exomelt also addressed important cost and safety concerns in making Ni_3Al . The process received a 1995 *R&D 100 Award* and has been widely adopted by industry.²

Ni_3Al and other intermetallics, especially iron and titanium aluminides, showed promise in a wide variety of industrial applications. The metallurgical

and mechanical properties of intermetallic alloys were to be improved by enhancing ductility, toughness, strength, creep and oxidation resistance. Intermetallic casting studies determined solidification behavior, mold interactions, fluidity, hot shortness, and other casting properties. Welding studies evaluated cracking susceptibility, weld properties, process development, and thermal and environmental aging behavior. Metalworking issues were addressed through hot ductility testing. The results of these studies were used to predict and adjust alloy compositions for specific industrial applications and fabrication techniques including the casting, welding and coating/cladding of intermetallics with properties suitable for conventional code-approved structures.

In 1992, a specific industrial application was identified to exploit the excellent thermal and corrosion resistance properties of Ni_3Al cast materials and reduce energy consumption.³ Nickel aluminide heat-treating trays (upper fixtures, lower fixtures, and support posts) were cast. Each tray assembly could carry 340 kg (750 lb) through a



furnace. Over 65 fixtures were successfully fabricated and installed in 1995 in a continuous carburizing furnace at GM Delphi Saginaw Steering Systems.

The nickel aluminide furnace assemblies provided greater carburization and oxidation resistance, as well as higher elevated temperature strength and creep strength than steel alloys. The trays lasted more than three times as long, reducing both scheduled and unscheduled down-time considerably. In addition, the lower mass of the assemblies reduced energy requirements for heat-treating by 11% and continue to save over 60 million Btu annually at the Saginaw plant. If utilized across the entire heat treating industry, roughly 30 trillion Btu could be saved annually in the United States.

In 2000, a Ni_3Al application was initiated that required both the casting and welding of intermetallics to make large industrial furnace



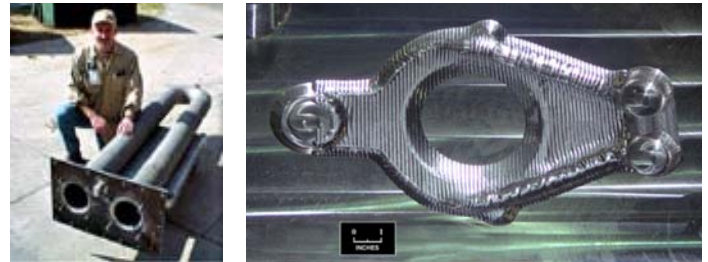
continuous caster rollers.⁴ Traditional roller surfaces warp, crack and blister. Ni₃Al properties minimize off-spec product that results from roller surface defects and minimizes furnace maintenance. Techniques to centrifugally cast large rolls, 17-inch diameter by 160-inch long, and to weld trunnions on both ends of the roll were developed.



Benefits derived from the use of intermetallics in this application include increased service life of rolls, elimination of the water cooling requirement, decreased materials rejection rate, and reduced energy use. Furthermore, efficiency is improved as a result of not needing to: (1) shut down austenitizing furnaces for frequent grinding of current rolls to remove blister, (2) shut down continuous casters to grind roll surfaces because of thermal fatigue cracking, (3) replace rolls as frequently in austenitizing furnaces and continuous casters and thus casting significantly fewer rolls, and (4) remelt and process out-of-specification steel plates due to marring by blisters on current rolls in the austenitizing furnaces or continuous cast systems. It is estimated that, if the technology was broadly adopted, the resulting energy savings will be over 32 trillion Btu per year.

A total of 101 rolls were fabricated and installed at the Burns Harbor Plate Mill in 2002. These have provided over two years of uninterrupted superior service.⁵ Continuous operation at this mill has resulted in an additional 210 operational days, product yields of consistently high quality and a 35% increase in energy efficiency. A total of 215,000 tons of steel plate (3 times the amount of steel used in the Empire State Building) have been heat treated. Duraloy (an ORNL licensed manufacturer of Ni₃Al) will soon manufacture 110 new rolls for installation at another U.S. mill.

Project partners have advanced the development of other Ni₃Al applications that include both casting and welding techniques. Annealing furnaces frequently use radiant burner tubes that fail due to creep deformation and oxidation mechanisms. Ni₃Al tubes eliminate these failures. Forging dies built of cast Ni₃Al alloy can remain in service ten times as long as those fabricated from commercially used die material. Nickel aluminide forging dies have been used to successfully forge 100,000 pieces of a part known as a "brake spider."



New industrial applications of intermetallics are continuing to emerge. For example, cast or wrought high-alloy stainless steels used for ethylene furnace tubes are subject to coke buildup and carburization. Coke buildup results in lower furnace efficiency and productivity. Removal of coke from the furnace tubes is a frequent and energy-intensive operation. The hydrocarbon feed is stopped, and natural gas and air are fed into the furnace to combust the coke deposits. This operation results in the loss of the fuel value of both the natural gas and the coke. Elimination of the need for decoking could result in annual energy savings of over 200 trillion Btu while simultaneously improving the furnace productivity. The unique oxide surface chemistry of Ni₃Al hinders the rate of carburization and coke buildup. Use of Ni₃Al for ethylene furnace tubes and development of novel tube manufacturing and welding techniques are being investigated.⁶

FUTURE DEVELOPMENTS AND THE SUCCESS OF INTERMETALLICS WORK

Other intermetallic alloys developed at ORNL are showing promise in a variety of industrial settings. FeAl intermetallics have resistance to carburization and sulfidation that far exceeds that of most commercial metal alloys. Ni₃Si alloys have good mechanical properties coupled with excellent



resistance to oxidizing conditions, such as in sulfuric acid and seawater, and to ammonia at temperatures up to 900°C. Ni₃Al and TiAl are also being characterized and evaluated for potential uses and commercialization.

The intermetallic alloy development program at ORNL has contributed significantly to the understanding of intermetallic materials and processing technologies. The program has been characterized by outstanding research and effective coordination between basic and applied research organizations. Finally, collaborative interactions between DOE, ORNL and industrial participants (metal producers and end-users) have contributed to plant floor energy efficiency improvements through the implementation of innovative alloy compositions and processing methods.

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PATENTS

The Ni₃Al research work performed at ORNL is protected under 27 patents in the United States.

LICENSES

Six licensed companies are producing nickel-aluminide alloys for the manufacture of industrial components in the United States.

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