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EXO-MELT™ PROCESS FOR INTERMETALLIC POWDERS

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ABSTRACT

The methods of powder production for intermetallics are reviewed. An innovative method known as *Exo-Melt*™ is described for producing molten aluminides for gas- and water-atomization processes that require a molten metal stream. The *Exo-Melt*™ process is based on the effective utilization of the heats of formation of aluminides from their constituent elements. The *Exo-Melt*™ process principles are discussed along with a description of a furnace-loading sequence that uses the principles for practical applications. The benefits of the *Exo-Melt*™ process are compared with the problems associated with the conventional melting process.

INTRODUCTION

The intermetallic-based alloys are gaining importance because of their attractive properties. For example, the Ni_3Al-based alloys offer high-temperature resistance to oxidation, carburization, chlorination, and nitridation [1]. These intermetallics also offer good high-temperature strength as opposed to many commercially used stainless steels and some nickel-based alloys [1]. Similarly, the Fe_3Al- and FeAl-based alloys show excellent resistance to high-temperature oxidation, sulfidation, and molten salts [1]. For many applications of Ni_3Al-based alloys, melting and casting are acceptable and provide an economical manufacturing method. The Fe_3Al- and FeAl-based intermetallic compounds of body-centered cubic (BCC) crystal structure show relatively poor room-temperature ductilities in the coarse-grained cast structure. Powder metallurgy offers an alternative to the casting process to obtain fine-grain microstructures with acceptable ductilities.

The intermetallic powder-production methods have been reviewed by German and Iacocca [2] and are briefly reviewed here.

1. Chemical Synthesis. Very small powders are possible through the chemical precipitation route. High-oxygen contents are a major problem, and the chemical processing may not be environmentally friendly.

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2. Milling and Mechanical Alloying. The process starts with a stoichiometric ratio of elemental powders. On a microscopic scale, the repeated milling, cold welding, and fracture of particles produce the desired intermetallic powder. The homogenization that occurs during milling converts the initial elemental particles into an alloyed form over a long period of time. The mechanical alloying approach can form oxide dispersions and intermetallic-compound-based composites but suffers from problems of impurity pickup and being very slow and expensive.

3. Inert Gas Atomization. This process produces the formation of powder from molten metal using dispersed fine droplets that solidify during free flight. Inert gas atomization uses argon, helium, or nitrogen gas as a fluid for breaking up the molten metal. This process is very widely used commercially for the production of spherical powders of low-oxygen content of a large number of metals, alloys, and intermetallics.

4. Centrifugal Atomization. This process uses a fusion process coupled with a centrifugal force. The centrifugal force throws off the molten metal as a fine spray which solidifies into a powder. The plasma-rotating-electrode process (PREP) is the most common application of this concept. In this concept, a consumable electrode made from this desired material is melted at one end by a plasma arc. The electrode rotates at velocities up to 50,000 revolutions per minute under an inert gas. The method produces spherical powders of low-oxygen content and 250-μm particle size. A variant of PREP pours molten metal on a rapidly spinning disk. The resulting powder is quenched in helium at 10^5°C/s.

   The PREP requires the preparation of an alloy electrode, which may not be easily feasible. The pouring of molten metal from an external source onto a rotating disk is more versatile.

5. Plasma Atomization. An agglomerated powder is fed into a plasma torch where melting and rapid acceleration occur. A powder smaller than 30 μm can be generated via secondary impaction against a substrate. The high velocity and high temperature of the plasma arc result in a high superheat, making this approach especially useful for higher temperature intermetallics.

Among the methods mentioned above, the inert gas atomization and water atomization methods (where a liquid metal stream is impacted with high-pressure water) are the most commonly used for commercial production. For either gas- or water-atomization processes, the availability of liquid of the aluminide of choice is required with the correct chemical analysis and low-interstitial content (such as oxygen and nitrogen). The purpose of this paper is to describe the newly developed *Exo-Melt*™ process for the melting of nickel and iron aluminides.

EXO-MELT™ PROCESS

The *Exo-Melt*™ process is based on the principle that the formation of the intermetallic compounds from their constituent elements is exothermic. The heats of formation, the weight percent aluminum, and the melting points of selected aluminides are summarized in Table I. The heat released during the formation of an intermetallic compound can be used to carry out an enthalpy balance at a given temperature to determine the maximum attainable temperature and whether the intermetallic would be in liquid or solid state. The following enthalpy equations have been used to determine the state of the intermetallic with the crucible temperature in the range of 660 to 800°C:

$$\Delta H^r_{T_0} = \int_{T_0}^{T_{ad}} Cp dT \tag{1}$$

and

$$\Delta H^r_{T_0} = \int_{T_0}^{T_m} CpdT + f\Delta H_m \ , \qquad (2)$$

where

$\Delta H^r_{T_0}$ = the enthalpy of reaction at T_0,
Cp = the heat capacities of the product.

Equation (2) above takes into consideration the phase transformation accompanying melting of the product and its latent heat of fusion, ΔH_m. If the product undergoes melting below the adiabatic temperature, T_{ad}, the fraction in molten condition, f, can be calculated from Eq. (2). Equations (1) and (2) above assume adiabatic conditions, and T_{ad} in Eq. (1) provides an upper limit for the temperature. With an initial temperature of 660 to 800°C, the enthalpy balance of Eq. (2) indicates that the product will be in the liquid state. On the other hand, simple calculation of T_{ad}, based on Eq. (1), suggests that the maximum temperatures are close to the melting point, and molten product may appear only in the case of NiAl (see Table II).

Table I. Heats of Formation, Aluminum Contents, and Melting Points of Selected Intermetallics (thermophysical properties from refs. 3 and 4)

Intermetallic	Heat of Formation ΔHf_{298} (K cal/mole)	Weight Percent of Aluminum	Melting Point (°C)
Ni_3Al	–36.6 ± 1.2	13.28	1395
NiAl	–28.3 ± 1.2	31.49	1639
Ni_2Al_3	–67.5 ± 4.0	40.81	1133
$NiAl_3$	–36.0 ± 2.0	57.96	854
Fe_3Al	– 16.0	13.87	1502
FeAl	–12.0	32.57	1215
$FeAl_2$	–18.9	49.1	1164
Fe_2Al_5	–34.3	54.70	1171

Table II. Calculated Adiabatic Temperatures for Ni-Al Systems

Intermetallic	T_{ad}, °C
Ni_3Al	1270
NiAl	1638
$NiAl_3$	1120

It is important to realize that several other parameters, such as the interfacial contact area between nickel and aluminum, aluminum content, and particle sizes also decide the fraction of the molten product [5-8].

The *Exo-Melt*™ process is an innovative method of furnace loading to maximize the utilization of the heat of compound formation to the melting of the desired intermetallic. For example, to melt the Ni_3Al-based alloy, the furnace-loading sequence used is the one shown in Figure 1.

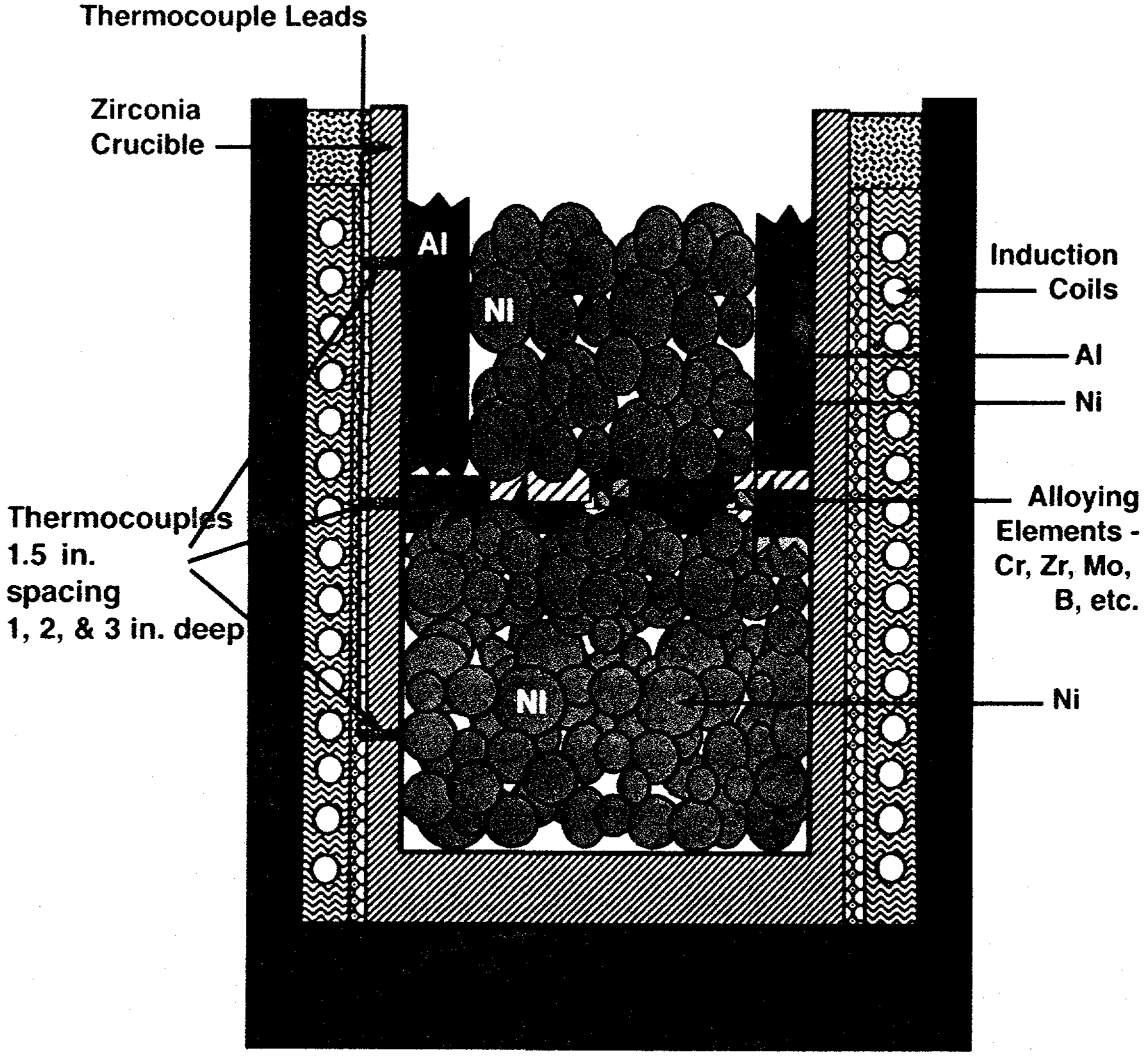

Figure 1. A schematic of the furnace-loading sequence employed for the *Exo-Melt*™ process to melt nickel aluminides. A similar arrangement can be used to melt iron aluminide also.

The aluminum melt stock is located vertically with nickel corresponding to NiAl next to it near the furnace top. The remaining nickel is located at the bottom of the furnace with alloying elements placed between the two layers. The aluminum is placed around the crucible so that the molten aluminum will react with the nickel to form NiAl on top. At a crucible temperature of 700°C or above the melting point of aluminum, NiAl forms as liquid. Liquid droplets of NiAl dissolve alloying elements and drip down to the remaining nickel. This division of nickel and aluminum melt stock allows the use of the heat of reaction of NiAl and raised the temperature to a signifi-cantly higher value than what could have been accomplished with Ni_3Al (see Table II for the maximum temperatures). If we used a furnace-loading sequence to allow formation of Ni_3Al, we could only have achieved a maximum adiabatic temperature of

1395°C at the crucible temperature of 700°C, since T_{ad} will be limited by the melting temperature of the product.

Systematic temperature measurement during the *Exo-Melt*™ process, carried out with the furnace-loading sequence shown in Figure 1, revealed that although the high-melting-point liquid of NiAl formed near the top, the overall bath temperature remained around 1250°C. Once the exothermic reaction was complete, additional power was provided to the furnace to raise the liquid-metal temperature to 1600°C for atomization or casting processes. However, if the melting process was carried out with the conventional wisdom of adding the solid aluminum to the molten nickel or nickel with alloy elements, the bath temperature increased from 1400 to 2300°C. Such an increase in temperature was accompanied by extreme brightness with white radiation, and a vapor cloud escaped from the crucible for several minutes. The oxidation of aluminum resulted in the vapor cloud, and part of the temperature rise may be attributed to the oxidation of aluminum. Such an increase in temperature also had additional detrimental effects of overheating the crucible above its use temperature, missing the alloy chemistry, and creating a potentially unsafe situation for the operator. The overall benefits of the *Exo-Melt*™ process as opposed to the conventional process are listed in Table III.

The *Exo-Melt*™ process described above for the melting of Ni_3Al-based intermetallics has also been successfully applied to the melting of Fe_3Al, FeAl, and NiAl at the Oak Ridge National Laboratory and commercial vendors. The *Exo-Melt*™ process carried out in the laboratory for 7.5-kg heats has already been extended to 300-, 1000-, and 2500-kg heats by several commercial vendors, and a total of 25,000 kg of Ni_3Al-based intermetallic has been produced to date. The melt quantities of Fe_3Al and FeAl are lagging behind Ni_3Al because their applications have not been fully established.

In most cases, the *Exo-Melt*™ process has been applied to virgin melt stock. However, a slightly modified furnace-loading sequence also permits the use of revert or scrap stock. A comparison of the chemical analysis of two 272-kg heats of nickel-aluminide alloy IC-221M, induction melted in air using the *Exo-Melt*™ process with virgin and revert stock, is presented in Table IV. This table shows a good chemical analysis match of the virgin and revert stocks with the target chemistry. Slightly lower zirconium in the revert stock resulted from not compensating for its loss during the virgin heat. Slightly higher oxygen of the revert melt is from the use of slightly oxidized revert as opposed to clear virgin stock.

SUMMARY AND CONCLUSIONS

The methods of powder production for intermetallics are reviewed. An innovative method known as *Exo-Melt*™ is described for producing molten aluminides for gas- and water-atomization processes that require a molten metal stream. The *Exo-Melt*™ process is based on the effective utilization of the heats of formation of aluminides from their constituent elements. The *Exo-Melt*™ process principles are discussed along with a description of a furnace-loading sequence that uses the principles for practical applications. The benefits of the *Exo-Melt*™ process are compared with the problems associated with the conventional melting process. The conclusions reached from this work comparing the *Exo-Melt*™ process with the conventional process are: (1) the *Exo-Melt*™ process is the best method for melting nickel and iron aluminides in air or vacuum; (2) this process allows the charging of the entire melt stock, including aluminum, at the beginning of the melt process; (3) this process uses approximately 50% of the energy required in the conventional process; (4) this process requires approximately 50% of the time required in the conventional process (the time saving comes from the effective use of the exothermic reaction and preventing overshooting, which requires extra time to cool to pouring temperature); (5) this process is inherently safe because the exothermic reaction is carried out in a controlled manner; (6) the energy and time savings of the *Exo-Melt*™ process have a potential to be nearly 50% less expensive than the conventional process; (7) the process has been moved from the laboratory stage to the commercial stage at several vendors; and

Table III. A Comparison of Melt Features of Conventional Process with *Exo-Melt*™ Process

Features	Conventional Process	*Exo-Melt*™ Process
Practical Aspects	Bath temperature is overshot from the exothermic reaction when aluminum is added to molten nickel alloy. Temperature increase/overshoot oxidizes alloying elements, affects crucible life, and delays the overall process because the melt has to set and cool.	A very practical method. Easy to load the furnace with all elements. The exotherm generates the maximum heat, which is shared with the solid and, thus, the heat is used for increasing the solid temperature. No temperature overshoot occurs, and melting takes place in a much shorter time.
Time to Melt	Unit time	One-half of conventional unit time
Power	Unit power (5.5 kW hours)	One-half to two-thirds of conventional power requirement (2.92 kW hours)
Safety	Temperature overshooting causes erosion of ceramic crucible, and can cause unexpected attack on induction coils by seeping through eroded area.	Avoids any potential safety issues
Cost	Melting cost is high because the exotherm is not used effectively. The oxidation of alloying elements can require either adding more of them or a large rejection rate resulting from poor repeatability.	Effective use of exotherm and chemistry control results in saving nearly one-half the cost of the conventional method.
	Unit cost	One-half the cost of the conventional method
Composition Control	Addition of aluminum to molten nickel causes the bath temperature to increase by 500 to 700°C. Such a temperature rise oxidizes the important elements such as boron, zirconium, chromium, and aluminum. Bath chemistry is missed, and oxide inclusions are mixed in with the alloy.	Effective use of the exotherm prevents overheating and, thus, chemistry is reproducible every time.
Oxide Inclusion Formation	Overheating of bath causes excessive inclusion formation	No excessive heating. Much less oxidation than conventional method.
Bath Temperature Control	No control	Real control
Crucible Life	The temperature overshoot by 500 to 700°C above the melting point of nickel causes excessive erosion of the crucible.	Uniform wear
	Excessive wear	Normal wear

Table IV. Comparison of Chemical Analyses of Two 272-kg Heats of Nickel-Aluminide Alloy IC-221M Melted in Air at Alloy Engineering &Casting Company (Champaign, Illinois), Using the *Exo-Melt*™ Process

Element	Weight Percent		
	Target	Heat E2153[a]	Heat E2155[b]
C	--	0.013	0.012
S	--	0.002	0.002
Si	--	0.04	0.09
Ni	81.146	*c*	*c*
Cr	7.74	7.70	7.75
Mo	1.428	1.44	1.48
Ti	--	0.01	0.01
Al	7.981	7.94	7.81
B	0.008	0.009	0.009
Zr[d]	1.697	1.56	1.35
N	--	0.012	0.016
O	--	0.012	0.022

[a] Heat melted from virgin stock.
[b] Heat melted from one-third virgin stock and two-thirds revert consisting of broken tray castings and gating.
[c] Balance.
[d] One-and-a-half times amount of zirconium was added in the melt stock to reach the target composition.

(8) this process has moved the commercial applications of nickel and iron aluminides as castings and powder metallurgy parts forward.

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