Multi-Component Master Alloys for Titanium

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Abstract

Master alloys for the titanium industry have evolved from simple binary Al-X alloys into a wide range of multi-component specialty alloys with as many as six or more elemental components. Most of these alloys are produced in one step by alumino-thermic (“thermite”) reduction reactions. In this paper, we present the thermochemistry of these alloys, the flexibility and range of the underlying thermite process, and some limitations imposed by that process. The operational advantages of multi-component master alloys are discussed, as well as circumstances in which such master alloys may not be the preferred material(s). Some alternatives and options for future work are presented.

Introduction

As the titanium industry grew in the 1950’s, the value of key alloying elements such as vanadium, aluminum, molybdenum and chromium was quickly established. However, these elements presented problems in alloying with titanium in that they are either much higher in melting point than titanium, differed dramatically in density, or were not readily available in sizes and forms that would dissolve quickly in the VAR re-melting process. To address these problems, master alloys were developed specifically for the emerging titanium industry. Initially, these were simple Al-X binary alloys, where X was vanadium, molybdenum, chromium or niobium. These alloys have melting ranges close to or below the melting point of titanium, densities much closer to that of titanium, and can be produced in sizes that minimize segregation in compacts and dissolve quickly in liquid titanium. These binary alloys grew up with the titanium industry and are still the major sources of new vanadium, molybdenum, chromium and niobium units flowing into the industry.

As the titanium industry developed more complex alloys, master alloy producers responded with multi-element alloys such as Ti-17 (6 or 7 elements), 6242 and 6246 (4 or 5 elements), Ti-5-1-1-1, Ti-5-5-5-3, as well as an array of proprietary alloys. Nominal compositions for some of the master alloys for these titanium alloys are shown in Table 1, below. While there are several ways to produce these complex master alloys, they each can be produced by a single-step alumino-thermic reaction.

Table 1. Multi-Component Master Alloys

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<tr>
<th>Alloy/Element</th>
<th>Al</th>
<th>V</th>
<th>Mo</th>
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<th>Zr</th>
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Alumino-Thermic ("Thermite") Reactions

An alumino-thermic reaction is a reaction between aluminum, a strong reducing agent, and a metal oxide less stable than alumina to produce a liquid metal or alloy and a liquid slag. The original "thermite" reaction was probably the reaction of powdered aluminum with iron oxide to produce liquid iron and a liquid aluminate slag. The reaction initially was used to weld iron or steel parts in the field. The excess heat released during the reaction raises the temperature of the reaction products so no other heat sources are required. This exothermic reaction has been expanded to a range of metal oxides and is the basis of much of RAI’s master alloy production.

Typical thermite reactions at RAI include Al-Mo, Al-V and Al-Cr. The basic reactions are:

\[ 2\text{Al} + \text{MoO}_3 \rightarrow \text{Mo} + \text{Al}_2\text{O}_3 + \Delta \]  \hspace{1cm} (1)

\[ 10\text{Al} + 3\text{V}_2\text{O}_5 \rightarrow 6\text{V} + 5\text{Al}_2\text{O}_3 + \Delta \]  \hspace{1cm} (2)

\[ 2\text{Al} + \text{Cr}_2\text{O}_3 \rightarrow 2\text{Cr} + \text{Al}_2\text{O}_3 + \Delta \]  \hspace{1cm} (3)

where \( \Delta \) represents heat given off by the reaction. In the above sequence the heat generated is (1)>(2)>(3). \( \Delta \) can be approximated by the difference in the enthalpies of formation of \( \text{Al}_2\text{O}_3 \) and the metal oxide being reduced. Over forty years ago our founder, Dr. Fred Perfect, found thermite reactions had sufficient available heat to reduce the oxide(s) and melt the metallic alloy and slag when the ratio of \( \Delta \) to the total charge weight fell within a fixed range. This generalization holds because most metallic oxides and metals have similar heat capacities and are condensed phases. Also, about half of the reaction products are an alumina-rich slag. Based on this concept, we can combine a number of metal oxides to produce complex master alloys in a single-step process. Thermal “boosters” or heat sinks can be added to keep within the desired energy range, and to allow more extensive alloying.

In most cases, the heat released by the reaction is sufficient for other metals or elements to be added as minor constituents in a complex master alloy. Other metals subject to thermite processing include silicon, iron, manganese, tin, titanium and zirconium. The titanium and zirconium are usually minor elements in a master alloy, although RAI does produce a master alloy with 40% Al and 60% Zr.

An excess of aluminum is used to lower the density and melting range of the master alloy. As can be seen from the binary phase diagrams below, aluminum has a very strong affect on the melting range of the metals of interest, and forms intermetallic compounds that make the alloys friable. Nickel has a similar affect on melting ranges (but not necessarily density), Figure 4, and has such a strong affect on the thermodynamic activity of the more reactive metal (vanadium, in this example) that residual aluminums can be below 1%. In the other extreme, high levels of reactive metals such as zirconium in the alloy demand higher levels of aluminum to drive the reactions and control residual oxygen contents.

Fluxes such as lime are used to lower the melting range and viscosity of the slag to further improve separation of the metal and slag. Finally, the kinetics of the reaction may be adjusted using
proprietary techniques to avoid very slow reactions (which lose too much heat to the surroundings) and over-rapid reactions (which may become explosive or damage the containment vessel).

By combining these simple binary reactions in different proportions we can produce alloys with a very broad range of compositions while retaining the fundamental simplicity, consistency, material efficiency and cleanliness of the thermite process. Once a “recipe” is established, heat-to-heat variances are extremely small, often less than the analytical uncertainty of the elements sought.

**When to use Multi-Component Master alloys**

Multi-component master alloys are particularly advantageous in initial production of new or modified complex titanium alloys. The multi-component master alloys can be tailored to the mill’s desired analysis, so a minimum number of materials are needed to reach the final composition. This simplifies operations, particularly when volumes are limited. Most multi-component master alloys are oriented to virgin heats. When large volumes of scrap alloy become available, multi-component master alloys become less advantageous since they are not matched to the available scrap.
While master alloy producers are constantly seeking lower-cost metal oxides suitable for the process and product requirements, the limited trading volumes of some oxides has led to situations where the cost of a metal as oxide has approached the cost of the elemental metal and the metal oxide may even be more costly than the elemental metal as scrap. In these situations, it may be more cost-effective to add the metals as elemental metals or scrap, in combination with a simplified master alloy. Tin and zirconium are two such elements. Each is compatible with titanium melting practices and available in sizes suitable for compaction and melting. The addition of new melting and re-melting techniques also changes the acceptance criteria for melt stocks. This makes some scrap and elemental additions economically attractive and physically acceptable.

At Reading Alloys we also have observed that a multi-element master alloy is not always the best choice for the job, even when requested by the customer. Some years ago we produced a tightly-specified multi-component master alloy for a customer, but we observed that by making two less-complex alloys not only could the component and tramp element tolerances be tightened, but the cost could be substantially reduced. The customer adopted the two-alloy approach.

Multi-component master alloys also are advantageous for in-situ formation of complex titanium alloys by powder metallurgy. Multi-component master alloys can be sized to match the titanium powder, reducing segregation that may be a problem with powders of differing sizes and densities. These powders also can be used in direct forming operations such as laser or plasma forming. Many of these alloys may be sized to –100 mesh or finer.

**Conclusions**

Multi-component master alloys can provide an efficient, cost-effective and very consistent way to add multiple elements to create complex titanium alloys. The sizing, melting range and density are compatible with all common melting techniques for titanium and its alloys. In producing these alloys by single-step thermite reactions, the inherent cleanliness, consistency and process efficiency of alumino-thermic reactions are used to maximum advantage. These alloys can be customized to meet particular customer requirements.

**References**


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Objectives of Master Alloys in Titanium

1. Lower the density of additive to near titanium density
2. Lower melting range of additive to near titanium melting range.
3. Provide additive in a physical form compatible with titanium processing.
4. Provide additive in a potentially lower-cost form.
Basic Thermite Reactions

\[ 2\text{Al} + \text{MoO}_3 = \text{Mo} + \text{Al}_2\text{O}_3 + \Delta \quad (1) \]
\[ 10\text{Al} + 3\text{V}_2\text{O}_5 = 6\text{V} + 5\text{Al}_2\text{O}_3 + \Delta \quad (2) \]
\[ 2\text{Al} + \text{Cr}_2\text{O}_3 = 2\text{Cr} + \text{Al}_2\text{O}_3 + \Delta \quad (3) \]
\[ \Delta = \text{Excess Heat/Gram}: (1) > (2) > (3) \]

The process is very flexible, with many other suitable reactions.
Process Control Keys

1. Combine thermite reactions to achieve desired chemistry
2. Keep excess enthalpy/gram within prescribed range
3. Use “boosters” or “heat sinks” to adjust excess enthalpy
4. Control reaction kinetics to achieve stable reaction rate
5. Consistent reactions lead to consistent master alloys
6. Add other elements to customize alloys
## Multi-Component Master Alloys for Titanium

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When to Use Multi-Component Master Alloys

- Initial production of new or modified complex Ti alloys
- Virgin heats of complex alloys
- When economically advantageous compared to alternative materials such as scrap or elemental additions.
- When heat-to-heat consistency is critical
- In-situ formation of complex alloys via powder metallurgy
When Multi-component Alloys are Contra-Indicated

- Suitable lower-cost alloy or elemental additions are available for the melting technique
- Combinations of binary or ternary alloys may be more cost-effective than a multi-component master alloy
- Melting is dominated by scrap rather than virgin materials
- Powders are required to be pre-alloyed, rather than formed in situ
Conclusions:

Complex, multi-component master alloys are the pinnacle of single-stage thermite technology.

They are not suitable for every application, but they can offer reliability, consistency and cost-effectiveness with the cleanliness, flexibility and material efficiency characteristic of the thermite process.