

Basic Ceramic Considerations for Lost Wax Processing of High Melting Alloys

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The growing demand for high melting alloys has led to the need for increasingly more refractory mold materials for the lost wax process. These materials must sustain their chemical, as well as mechanical stability in order to produce high quality castings. This paper initially outlines the mold requirements for a number of high temperature alloys. Ceramic-liquid metal interactions, oxygen affinity, as well as aqueous solution chemistry for multi-component refractory systems will be discussed. Next, guiding principles in practical mold design for the above alloys will be outlined.

INTRODUCTION

The demand for casting high melting alloys has grown in recent decades due to attractive thermal, mechanical and chemical properties of such alloys. Since its initial development in late 1940's early 1950's, the lost wax process has enjoyed a healthy growth in casting of high melting alloys in many markets such as aerospace, prosthetic, jewelry, automobile parts, hand tools and leisure equipment.

The casting of high melting alloys presents a special problem due to the high reactivity of these materials in the molten state. Reactivity of high melting alloys requires special shell-making practices to reduce the introduction of casting defects. Shell materials need to be of sufficiently high refractoriness. As a general practice, a high refractory facecoat slurry is normally applied to the wax pattern to improve refractoriness. Shells need to have sufficient high temperature mechanical stability to ensure dimensional accuracy of cast parts as well. Therefore, shells should neither densify nor creep throughout the process. The need for use of high refractory shell molds imposes additional challenge to high melting alloy casting. Slurries made of high refractory flours may have a very short lifetime. Lack of sufficient slurry life can make the shell-making process more costly. Moreover, the quality of shells may become unsatisfactory even in batch processes. The purpose of this paper is to outline a methodology for design of ceramic shell mold systems suitable for casting high melting alloys.

THERMODYNAMIC CONSIDERATIONS

The general chemical reactions that lead to metal - mold reaction can be classified as being of the following types:

- 1 $M_1O_x + xM + yQ$
- 2 $M_1O_x + zMA = MA_xO_z + g + xM$
- 3 $M_1O_x + zMA = MA_xO_z + xM$
- 4 $M_1O_x + zMA = MA_xM_wO_z + wM$
- 5 $M_1O_x + xM/g + yQ$
- 6 $M_1O_x - M_2O_z /$

where M_1O_x denotes an oxide, M and Q dissolved metal and oxygen in the alloy respectively, MA an

element in the alloy, and g a gaseous species. The discussion that follows may also be extended to include carbides, nitrides, sulfides and borides as well.

Most high temperature molten alloys dissolve molds to some extent. Reaction 1 describes dissolution of shell material into the liquid metal. The change in free energy for reaction 1 is equal to $\Delta G = \Delta G_f^{\circ} M_1O_x - RT \ln a_M^x a_O^y$ where a_M and a_O are the activity coefficients of M and O in liquid metal respectively. Calculating the precise value of ΔG in equation 1 is difficult. The activity coefficients are unknown, the conditions are non-standard, and the shell material is normally inhomogeneous. However, as a first order approximation, the solubility of various oxides in molten alloy decreases as $\Delta G_f^{\circ} M_1O_x$ becomes increasingly negative¹. ΔG_f° for some commonly used refractory materials, as well as oxides of some high temperature metals are given in Figure 1. Data in Figure 1 suggests that it is unlikely that high refractory oxides dissolve into molten Pd or Pt metals according to equation 1. However, casting of Ti in oxide shell molds such as Al_2O_3 or ZrO_2 will result

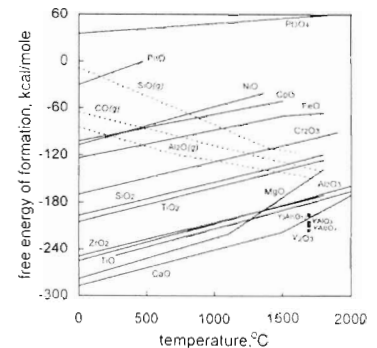
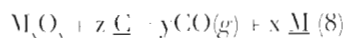


Figure 1: Free energy of formation for some refractory oxides, and the oxides of some high melting temperature metals.

in substantial dissolution of oxygen and metal into molten Titanium. According to Figure 1, ΔG_r° of both Al_2O_3 or ZrO_2 are more negative than TiO_2 . However, ΔG_r° of sub-oxides of Ti (*i.e.*, TiO) are more negative than the above oxides. Therefore, one can predict that molten Ti is apt to react with mold materials. There are a few known refractory oxides for which the ΔG_r° is more negative than $\text{TiO}^{2,4}$. Among these refractories, Y_2O_3 has received particular attention as a serious candidate for Ti casting^{5,6}. Figure 2 compares the level of surface oxygen (Δ case) on cast titanium versus the type of oxide used as facecoat material. Experimental details are given elsewhere⁷. The above data clearly shows the usefulness of ΔG_r° argument in evaluating the solubility of shell materials. Similar arguments have been used to show the solubility of oxides in superalloys as well^{8,9}.

Reactions 2,3 and 4 characterize the reaction of the molten metal with the mold. Reaction 2 becomes especially important when the gaseous reaction products have an significant equilibrium vapor pressure. Some of the most stable vapor oxide species commonly encountered in high melting alloys are listed in Figure 1. An example of reaction 2 is rapid decarborization of NiTaC alloy based on the following reaction:

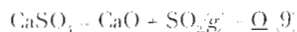


Reaction 3 involves reduction of the mold by the metal to form another metal oxide. This type of reaction can also be predicted by comparing the ΔG_r° of mold material and oxide of molten metal. Thus, ignoring the contribution of activity coefficients, reaction 3 can be prevented/promoted by

using mold materials having a ΔG_r° substantially more/less negative than oxide of molten metal respectively. A good example of reaction 3 is the reaction between Ti, Al or In in superalloys with the mold oxides⁵. The above reactions normally produce thin layers of molten metal oxide at the metal-mold interface. Such interfacial reactions are commonly stable and may be beneficial for the cast part by hindering further reactions between mold and the molten metal. Another example of reaction 3 is the reaction between Ti and the mold oxides in molten Ti alloys to form TiO or TiO_2 . The above oxides are frequently not seen because these oxides dissolve rapidly in metal.

Molten metal may form double oxides with the mold material (reaction 4). An example is the reaction between Al and rare earth oxides. ΔG_r° of rare earth oxides is normally more negative than ΔG_r° of alumina. Thus, ΔG_r° of double oxides comprised of Al_2O_3 and a rare earth oxide are more negative than pure Al_2O_3 ¹⁰. For example, as shown in Figure 1, ΔG_r° of double oxides $\text{Y}_4\text{Al}_5\text{O}_{12}$, YAlO_3 and YAl_2O_9 are more negative than ΔG_r° of Al_2O_3 . Consequently, molten Al is more reactive with rare earth shell molds than it appears to be on the basis of single oxide ΔG_r° data.

Reaction 5 characterizes a gaseous reaction product in a cast part. An example of such reaction is shown by Ingo and co-workers¹¹. The authors show that CaSO_4 - SiO_2 mold materials used for casting alloys of Au or Pd decomposes according to the following reactions:



The produced oxygen dissolves into the alloy and forms oxides with the minor alloying elements

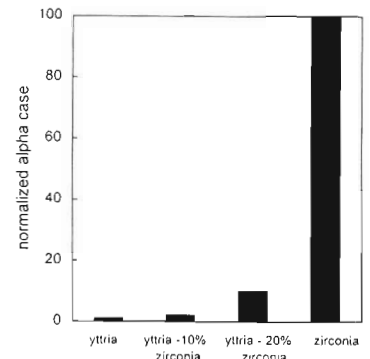


Figure 2: Normalized alpha case of one inch Ti cast as a function of shell mold refractory. Yttria-zirconia refractories were fused. Shurries were made with 5 weight% silica binder.

such as Cu, Ag and Zn. The above reaction is then further catalyzed by the presence of SiO_2 and the formed oxides in the melt. The result is the formation of a heavy concentration of SO_2 gas in the cast.

Reaction 6 represents solid to liquid transformation of ceramic components in the shell mold. Formation of liquid phase is detrimental to a cast part in a number of ways. Solid to liquid transformation does not contribute to a substantial change in the ΔG_r° of oxides¹². However, formation of liquid phase increases the oxide mobility. Consequently, the kinetics of reactions increases. Formation of liquid phase lowers the

Table 1 Melting Temperature for selected Metals and refractory oxides

Metal	Melting Temp. °C	Ceramic	Melting Temp. °C
Ir	2410	magnesia	2852
Ru	2310	zirconia	2700
Pt	1772	calcia	2614
Ti	1660	zircon	2550
Pd	1554	yttria	2415
Fe	1535	lanthana	2307
Co	1495	alumina	2072
Ni	1455	titania	1830
Au	1064	silica	1720
Ag	961	calcium sulphate	1450

mechanical stability of the shell mold as well. Surface erosion, part deformation and metal penetration into the mold can be among the many negative consequences of liquid formation. Table 1 compares the melting temperature of commonly used refractory oxides with some high temperature metals. As a general rule, shell material should be chosen such that its melting temperature is considerably above the melting temperature of the metal. Ceramic shell molds are multi-component systems. Consequently, the onset of liquid phase formation generally is lower than the melting temperature of individual pure oxides. For example, addition of Y_2O_3 to SiO_2 reduces the onset of liquid phase formation from $1720^\circ C$ to $1660^\circ C$. Addition of Al_2O_3 to the above mixture will further reduce the liquidus temperature to $1370^\circ C$. The effect of fluxing agents needs to be considered as well. For example, conventional colloidal silica used in lost wax process may contain more than 0.6 weight % of Na_2O ¹⁵. The added Na_2O reduces the melting temperature of SiO_2 from $1720^\circ C$ to as low as $837^\circ C$.

MOLD SURFACE PENETRATION

Beside cast defects caused by chemical reactions between the mold and the molten metal, physical interaction between mold and molten metal can also cause cast defects. Positive rough surface defects may be produced when molten metal penetrates into a mold porosity. The interaction between shell pores and molten metal can be approximated by¹⁵

$$P = -2 \gamma_k \cos \theta / r \quad (10)$$

where P is the pressure necessary to force molten metal into a pore of radius r, γ_k is the surface tension of the molten metal, and θ is

the contact angle between the molten metal and the shell. Contact angles $<90^\circ$ indicate capillary attraction. Molten metal wets the mold and penetrates into the pore without an applied pressure. Contact angles $>90^\circ$ indicate non-wetting condition, and applied pressure P is necessary to force the molten metal into the pore. Contact angle θ is related to surface and interfacial energies according to Young's equation¹⁵

$$\cos \theta = \gamma_{sv} - \gamma_{sl} / \gamma_{lv} \quad (11)$$

where γ_{sv} is the surface tension of refractory and γ_{sl} is the interfacial tension between the refractory and the molten metal. In order to promote metal penetration, γ_{sv} should be maximized and both γ_{sl} and γ_{lv} should be minimized. Interfacial tension, γ_{sl} , is perhaps the most influential factor in the value of contact angle between molten metal and the mold. γ_{sl} normally becomes lower upon the occurrence of an interfacial chemical reaction. Therefore, high temperature reactive metal alloys such as Ti are more prone to cause metal penetration compared to less reactive metals such as Pt. Li¹⁵ has also shown that surface tension of an oxide is directly related to its ΔG_f° . The above author shows that contact angle between molten Co, Fe or Ni and a mold changes from about 85° to nearly 135° , as the refractory changes from Cr_2O_3 to an oxide with a more negative ΔG_f° , such as CaO.

Note that in equation 10, r, is in the denominator. Therefore, the larger the radius, the smaller pressure is required to force the metal into the pore. Porosity in a lost wax shell mold is normally very fine. Therefore, in most situations, mechanical penetration of metal into the mold does not happen. However, under some conditions metal penetration becomes

possible. Occurrence of chemical reaction between metal and mold normally reduces contact angle below 90° and metal penetration becomes favorable. Moreover, formation of either liquid phase or occurrence of microcracks on the surface of the shell mold drastically increases the effective radius of porosity. Casting method can also have a major effect in promoting metal penetration. In static casting, P is primarily due to metallostatic head of the metal in the mold. However, metal pressure substantially increases in centrifugal casting and frequently causes metal fining in microcracked molds.

SHELL MAKING CONSIDERATIONS

Proper selection of shell mold material is vital to the successful production of high quality cast parts. However, it should be noted that the actual reaction of molten metal with the mold material is much rarer than supposed. Much of observed defects in a cast part are actually a result of faulty shell mold production. In the following, some of the fundamentals of shell making will be considered.

The lost wax shell making process for high temperature alloys can be summarized in the following generalized steps.

- A. Multi-component slurries are prepared. These slurries are composed of a refractory system and a binder system. The binder system includes at least one condensable inorganic binder.
- B. Facecoat layer(s) are constructed through dip coating and stuccoing of an organic based pattern.
- C. Shell mold is constructed either by applying multiple dip coatings, or by gelling a solid

body of slurry around the facecoat layers.

If the slurry is an aqueous based slurry, the binder system generally includes a nano-meter size colloidal silica binder. If the slurry is a non-aqueous based slurry, the binder system is generally a silicon alkoxide. In either case, condensation of binders causes permanent siloxane bond formation upon shell drying¹⁶.

a. Aging of slurries

Because of the very nature of the shell making process, slurries go through aging. As slurries age, they lose their useful properties, and either become useless, or jeopardize the quality of lost wax shell molds.

There are at least two reasons why lost wax slurries age⁷. First, different components in a slurry may interact with each other, and cause aging over time. For example, it has been shown that in aqueous slurries, the soluble species originating

from each component of a slurry may specifically adsorb on the surface of other components^{17,18}. Surface adsorption may modify surface properties and cause aging over time. The degree of interaction among different components of a slurry differs from one slurry to another. For example, as shown in Figure 3, aqueous MgO slurry with colloidal silica binder at pH 10.5 ages very rapidly and gels in less than an hour. Y_2O_3 slurry under similar conditions gels in a few hours. On the other hand, Al_2O_3 slurry under identical conditions remains stable for many months. Details of experimental procedures are given elsewhere^{2,17}. The above aging mechanism is shown to be the dissolution of polyvalent cationic ions from oxide flours, and then preferential

adsorption of these ions on the surface of negatively charged colloidal silica particles^{2,17}.

The above diversely different aging behaviors among slurries can be predicted from a prior knowledge of the speciation diagram for each flour in aqueous environment. Figure 4 compares the dissolution of yttria, magnesia and alumina. For simplicity, only the most dissolving ion specie from each flour is compared. At pH 10.5, dissolution of alumina is about five orders of magnitude lower than that of yttria. Consequently, stable alumina slurries can be made at pH 10.5. On the other hand, magnesia dissolves over three orders of magnitude higher than yttria at pH 10.5. Consequently, long lasting stable magnesia investment casting aqueous slurry can not be produced at above pH. One method to increase the lifetime of slurries is to prepare the slurries at higher pH values. As the pH goes up, the concentration of dissolving ions decreases (Figure 4) and consequently, slurries do not age as rapidly. For example, as shown in Figure 3, lifetime of Y_2O_3 slurry can be extended to about two months by simply adjusting the slurry pH to 11.

In slurries where silicon alkoxides are used as binder, an increase in pH, as the result of dissolution of components, and/or water moisture adsorption from the environment, normally reduces the slurry lifetime. Aging behavior of these slurries may differ depending on the amount of dissolution of components in the slurry. For example, rare earth ethyl silicate slurries may age very rapidly and become useless in less than a few hours. Alumina based slurries age slower and in a similar environment may last a few weeks. On the other hand, in some slur-

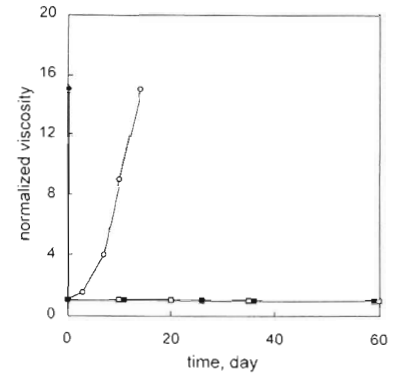


Figure 3: Normalized viscosity as a function of time. \square represents alumina-silica slurry at pH 11, \blacksquare represents yttria-silica slurry at pH 10.5, \circ represents yttria-silica slurry at 10.5, and \bullet represents magnesia-silica slurry at pH 10.5

ries, such as zircon or fused silica slurries, the above types of interactions are even less severe and slurries may last for many months. In general, one may draw a symmetry between aqueous slurries and their ethyl silicate counterparts. Flours that produce aqueous slurries with short / long life, produce ethyl silicate slurries with relatively short / long life as well. Other non silicon based alkoxides normally go through hydrolysis and condensation reactions very rapidly¹⁹. For this reason, despite their high refractoriness, non-silicate alkoxides have not found

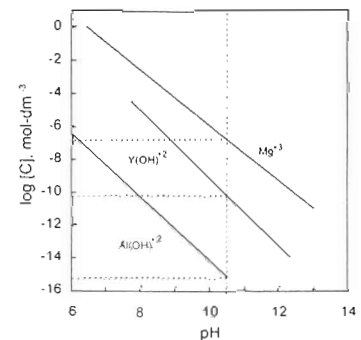


Figure 4: Ion concentration diagrams as a function of pH

popularity as binders in casting industry.

Besides aging due to component interactions, there is yet another reason why investment casting slurries age⁷. Inorganic binders such as colloidal silica are chemically reactive. They permanently bond as the result of siloxane formation upon surface contact. While in the slurry, the possibility of direct surface to surface contact between colloidal silica particles is low, due to the ionic cloud around each particle (diffused double layer). However, once these particles dry, their surfaces will contact and bonding will occur. Drying of particles may occur during many stages of the shell making process. Any stage of the process that promotes formation of a slurry-air interface could potentially cause evaporation of surface water and bond formation between colliding particles. For example, after a part is dipped in a slurry pot, it is removed and the excess slurry allowed to drip off the shell, back into the pot. As the slurry is dripping back to the slurry pot, a large area of slurry-air interface is formed that promotes slurry aging.

The above two factors cause lost wax slurries to age over time and lose their usefulness. Slurry aging due to component interactions may be reduced by properly formulating the slurry. However, solutions to slurry aging due to the formation of slurry - air interface is not sufficiently explored and presently handled only through careful quality control⁷. In a recent work, Yasrebi et al have shown that slurry aging can be substantially reduced by the "Infiltration Method" in shell making processes²⁰.

b. Mechanical Properties

Mechanical properties are

among the most important properties in a shell mold. Without proper design of mechanical properties, quality and price of a cast part can drastically suffer. This is especially true for casting of high temperature alloys, where molds normally have one or two facecoat layers of high refractory materials. Facecoat layers are thin and susceptible to stress cracks, high temperature erosion and deformation.

The main source of shell layer green strength is siloxane bonds formed by the condensation of silica binder. One way to increase the strength of a shell layer is to add more binder to the slurry. A series of zircon slurries were made with varying amount of silica binder. The exact formulation and procedure is shown elsewhere²⁰. Test bars were then made and the green strength of the bars was measured.

The general trend in the green strength is shown in Figure 5. An increase in the concentration of silica binder results in an increase in green strength of the shell to a point. After a critical binder concentration, shell strength decreases. The reason for the existence of a maxima in the strength curve may be explained as follows^{21,23}. Below the critical concentration, there is simply not enough binder between particles to bind particles efficiently. Above the critical concentration, due to a large concentration of binder in between flour particles, flours are unable to touch surfaces when the shell dries. Furthermore, as the binders in between the flour particles dry, a large amount of shrinkage occurs, producing microcracks that eventually contribute to a decrease in the strength. The curve in Figure 5 may be moved upward to some extent by optimizing a number of variables

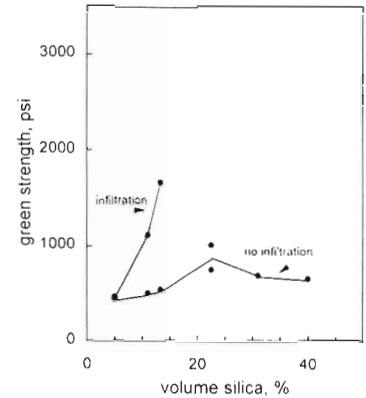


Figure 5: Green Strength as a function of volume concentration of silica in the shell. Infiltration line data are green strength values obtained after shell made from slurry with a 5 volume % silica was infiltrated with colloidal silica binder.

such as surface area, size and the morphology of binder or flour particles^{21,23}.

High temperature properties of a shell layer, such as hot strength and creep, closely follow the same trend observed for shell green strength, illustrated in Figure 5. Hot strength values also go through a maximum at the point of silica critical concentration. On the other hand, the creep curve goes through a minimum at the point of silica critical concentration²⁰.

It is normally desirable to design slurries at the critical concentration of silica, where shell strength is at maximum and creep is at its minimum value. However, if the reaction between the molten alloy and the relatively low refractory silica becomes a concern, then concentration of silica is reduced. An example of such a case is casting of Ti alloys (reaction D). Facecoat slurries for Ti shell molds have a very low concentration of silica binder, which increases the possibility of erosion, crack and deformation of the facecoat.

One may use an alternative shell making method to substantially increase the green strength at lower silica binder contents. Test bars from zircon slurry with only 5 volume % colloidal silica binder were constructed. Dry bars were then infiltrated with colloidal silica for three hours. Some of the infiltrated bars with colloidal silica were infiltrated for a second time after being dried. The results are shown in Figure 5. Bars that were infiltrated once showed green strength of 1100 psi. Total amount of silica in the shell was calculated to be at 11 volume %. After the second infiltration, silica content went up to 16 v/o and green strength became 1650 psi. It is shown that using infiltration method, green strengths in excess of 3000 psi can be obtained²⁰.

Reasons for the above increase in strength by the infiltration method can be speculated based on the explanation for the existence of a maxima in strength curve²⁰. As the amount of binder in the slurry increases, the total bonding between flour particles increases and the green strength goes up. As it was discussed earlier, the bonding between particles increases only up to the point of maximum in Figure 5. As the slurry dries, some part of the binder will dry inside the cavity between particles and does not contribute to bond formation between particles. On the other hand, during the infiltration process, flour particles are already in contact and bonded together. Once the additional binder is infiltrated inside the porous shell, binder liquid is drawn to the neck region between particles due to capillary action. As the binder dries, it dries at the neck region and further increases bonding between particles.

Summary

Ceramic molds for casting of high temperature alloys have to satisfy certain requirements. Refractory materials in the mold should retain their chemical stability in contact with molten alloy. Mold materials, as a first order approximation, should have ΔG_f° comparable or preferably more negative than the oxides of molten alloy. In addition, the mold should have high enough liquidus temperature in order to retain its mechanical stability at the cast temperature.

Besides materials requirements, proper processing of molds should also be exercised. Slurries should be prevented from excessive aging. Electrochemical properties of individual components in the slurry should be reviewed in order to ensure minimal component interactions. Slurry pots should be monitored regularly to prevent excessive aging due to binder agglomeration at the air-slurry interface. Finally, mechanical properties of the shell need to be designed to ensure defect-free parts. Maximum strength and minimum creep can be achieved at the critical concentration of binder in the slurry. If it becomes desirable to reduce the amount of silica binder, then the infiltration method can be used to optimize strength and creep in a shell system.

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