THE INVESTIGATION OF MINOR ELEMENT ADDITIONS ON OXIDE

FILTERING AND CLEANLINESS OF A NICKEL BASED SUPERALLOY

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Summary

Effects of minor element additions on filtering were studied by examining filtered and unfiltered melts of UDIMET® Alloy 700B (U-700B) with small additions of hafnium, rhenium and yttrium. Comparisons were made by sectioning filters, EB-button raft measurement, and sessile drop melting. Results provided evidence that these additions influence the filtration of molten metal. The examinations of filter cross sections also provided a perspective which supports oxide flotation as the basic function of the filter system.

Introduction

High performance superalloys designed for fatigue resistance in turbine engine applications demand ultra-clean material processing. Liquid metal filtration, using ceramic foam filters, is an advancing technology which responds to this demand. An understanding of the phenomena involved in the filtering process is necessary to develop improved procedures. During the observation of current filtering practices, the presence of minor elements in superalloys appeared to influence the characteristics of filtration and filter efficiency.

Several authors including Sutton[1,2,3,4], Apelian[5] and Ali[6] have reported varying results on the effects of alloy composition and filtering techniques on inclusion removal and filter efficiency. This study was intended to examine filtration phenomena in present filtering processes and to determine how alloy composition affects filtration.

Experimental Design

U-700B is a nickel based superalloy which contains aluminum and titanium for precipitation hardening similar to alloys now being manufactured and processed using filtration technology. The alloy contains no rhenium, hafnium or yttrium and it was therefore used to make a systematic investigation of

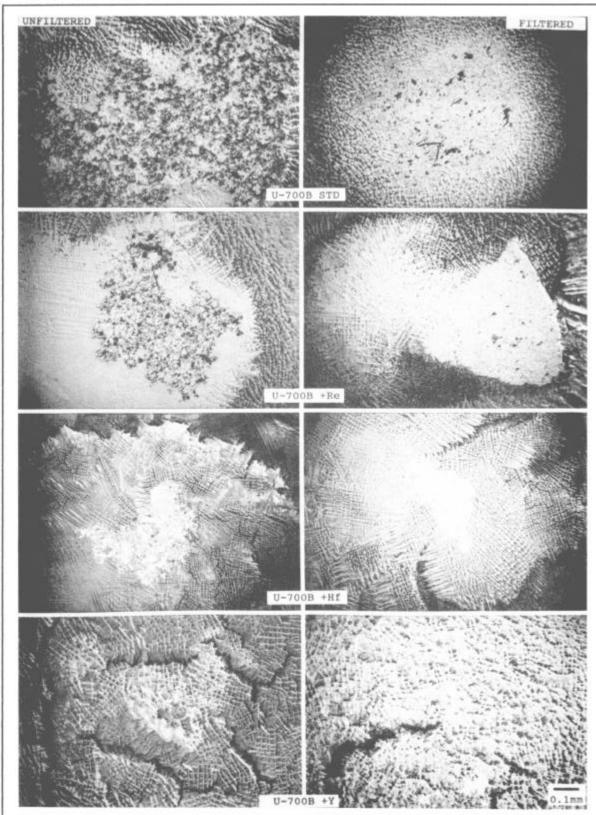®UDIMET is a registered trademark of Special Metals Corporation

Figure 1. Scanning electron micrographs of EB button rafts from tops of filtered and unfiltered ingots. Materials with low atomic number elements, e.g., aluminum, appear dark, and high atomic numbers, e.g., hafnium, appear light.

the effects of these elements on the removal of oxide inclusions by filtration. Rhenium, hafnium, and yttrium were chosen for study because they are minor elements used in recent years in advanced investment cast and cast-wrought alloys.

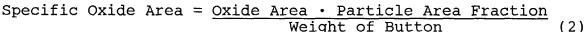| Table I Specific Oxide Areas and particle sizes for each of the unfiltered and filtered alloy modifications.							
		UNFILTERED			FILTERED		
		RATING	PARTICLE (μm)		RATING	PARTICLE (μm)	
ALLOY	RAFT OXIDE	cm²/kg	TYPICAL	LARGEST	cm²/kg	TYPICAL	LARGEST
STD TOP	Al	0.362	1-200	400	0.060	1-100	200
BOT	Al	0.050	1-200	400	0.091	1-100	200
AVE	Al	0.206	1-200	400	0.076	1-100	200
+Re TOP	Al	0.14	1-200	400	0.038	1-10	300
BOT	Al	0.05	1-200	400	0.057	1-10	100
AVE	Al	0.10	1-200	400	0.048	1-10	300
+Hf TOP	Hf	0.036	1-200	700	0.015	1-10	10
	Al	0.006	1-100	700	0.004	1-10	100
BOT	Hf	0.122	1-200	800	0.071	1-10	10
	Al	0.035	1-100	300	0.011	1-10	400
AVE	Hf	0.079	1-200	800	0.043	1-10	10
	Al	0.021	1-100	700	0.008	1-10	400
+Y TOP	Y	0.05	1-200	500	0.014	1-10	10
BOT	Y	0.125	1-200	500	0.028	1-10	10
AVE	Y	0.088	1-200	500	0.021	1-10	10

Rhenium was included in this study because difficulties were encountered in the past in EB cleanliness evaluations of Re bearing alloys. Experience has shown that oxides are difficult to sweep to the center of the button for subsequent analysis. About 1.0% rhenium is present in commercial alloys. Hafnium and yttrium were included because they are strong oxide formers and are expected to reduce Al_2O_3 and other less stable oxides. Hafnium concentrations of 1.0% are typical of several hafnium bearing alloys now manufactured. Yttrium has been used in a wide range of concentrations from as much as 1% in coating materials to as little as 0.05% in wrought superalloys. A concentration of 0.5% Y was used in this series.

Eight experimental heats with different minor element additions were vacuum induction melted (VIM) and poured with and without filters. The same lots of virgin raw materials were used for all melts in order to obtain consistent melt quality. The modifying elements were added to the base charge in a magnesia ram crucible. The filtered melts were poured through alumina pour cup assemblies containing high density partially stabilized zirconia (HDPSZ) foam filters. The filters were disks 76mm φ x 25mm (3" φ x 1") thick with an open pore size of 8 pores per cm (20 pore per inch). The filter assemblies were pre-heated to 1090°C (2000°F) for one hour before pouring. The pre-heated assemblies were transferred to the VIM furnace at the time of pour to minimize heat loss. The poured materials were collected in 75mmφ x 412mm (3"φ x 16.5") cast iron molds incorporating hot top insulation to improve ingot soundness. Ingots and pour assemblies were allowed to cool in vacuum before they were removed from the VIM furnace for further operations. The ingots were removed and sectioned for remelting in an EB button furnace. Procedures for EB button melting are described

elsewhere[7]. The rhenium modified unfiltered heat presented a problem due to insufficient filling of the hot top and, subsequently, the top of the ingot was sampled by sectioning off center to avoid the primary pipe. Cleanliness was assessed at the top and bottom of each ingot. Oxide rafts from filtered and unfiltered experimental alloys are shown in Figure 1. An oxide area measurement of each raft was made by a planimeter trace of the elemental x-ray maps from a scanning electron microscope. Oxides of Al, Hf, Y, Mg and Zr were detected. The latter two were only found in trace amounts and were not included in the measurements. The areas were initially normalized by the area fraction of particles in the raft, measured by a line intercept method.

$$\text{Particle Area Fraction} = \frac{\text{Particle Intercepts}}{\text{Total Intercepts}} \qquad (1)$$

These areas were again normalized by the weight of the EB button to give a specific oxide area, cm^2/kg.

$$\text{Specific Oxide Area} = \frac{\text{Oxide Area} \cdot \text{Particle Area Fraction}}{\text{Weight of Button}} \qquad (2)$$
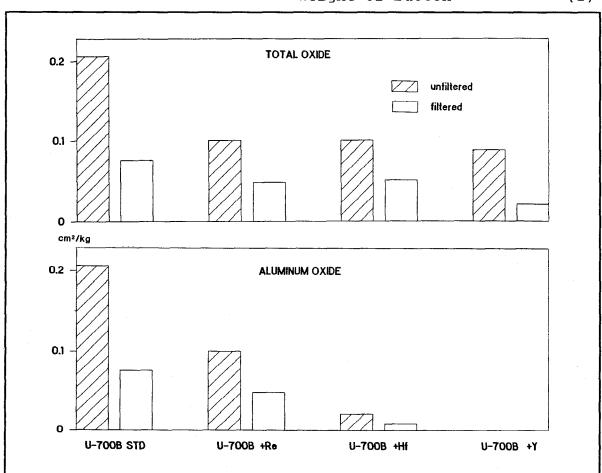

Figure 2. Graph of Specific Oxide Area of total oxide raft and aluminum oxide raft for unfiltered and filtered melts of each experimental alloy.

The filter/pour cup assemblies were disassembled and the filters were sectioned,mounted and metallographically polished. The polished surfaces were then coated with carbon to provide a conductive layer for examination in the SEM. The filter cross
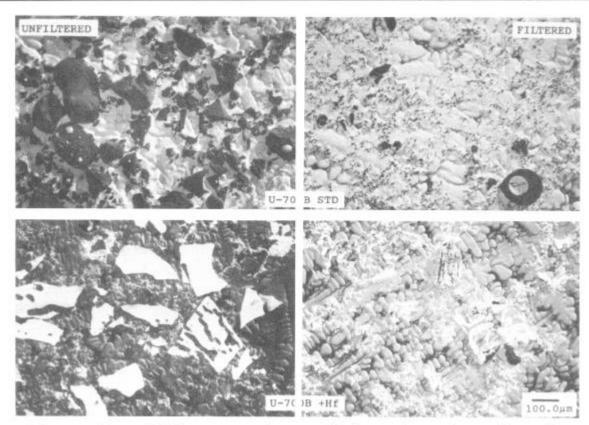
Figure 3. Differences in particle sizes in rafts of unfiltered and filtered standard grade and Hf-Modified U-700B.

sections were examined for oxide particles attached to filter spine surfaces, imbedded in the molten alloy within the filter and at the top surfaces of the filter. The size of the oxide particles were measured and their chemistries were determined by Energy Dispersive Spectroscopic (EDS) microanalysis.

Samples were taken from each alloy for chemistry including O and N analysis, Differential Thermal Analysis (DTA), and sessile drop melting.

Experimental Results and Discussion

A summary of the raft oxide data obtained in the SEM is provided in Table I. Figure 2 compares the cleanliness before and after filtration. All four alloys were cleaner after filtration. For the standard alloy and the rhenium modified U-700B only Al_2O_3 particles were found in the rafts. The hafnium modified alloy produced 80% HfO_2 particles and 20% Al_2O_3 particles in the rafts of both the unfiltered and filtered materials. The yttrium modified alloy produced Y_2O_3 particles and only a trace of Al_2O_3 particles in the rafts of the unfiltered and filtered melts. The amount of Al_2O_3 particles was significantly reduced by the minor additions of hafnium and yttrium, Figure 2. Cleanliness improvements were achieved before filtration by the additions of rhenium, hafnium or yttrium. The specific oxide areas were averaged for top and bottom ingot samples. Without filtering, the average specific oxide area for rafts of the modified alloys were approximately half of those for the rafts of the standard alloy. The rhenium modified alloy
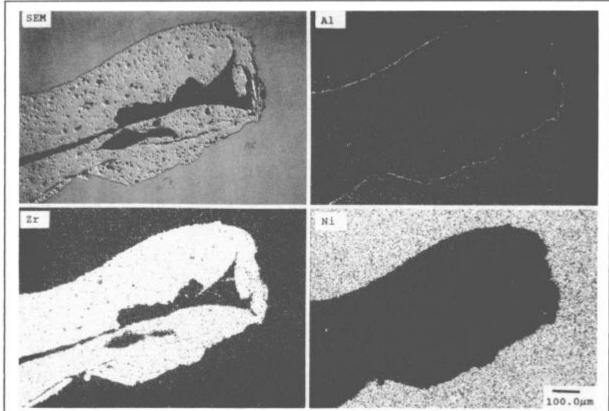
Figure 4. SEM photo and elemental x-ray maps of metal and filter solidified after pour. Example was taken from standard grade U-700B melt.

result was unexpected and may be due to problems in sampling the inadequately hot topped unfiltered ingot. Figure 3 demonstrates the reduction in typical particle size with filtration. This is important because studies have shown that particle size of inclusions is related to alloy fatigue properties[8]. The inclusion size in low cycle fatigue is inversely proportional to the number of cycles to failure.

There appears to be four mechanisms by which ceramic foam filters remove oxides from molten metal: 1) <u>Mechanical sieving</u> which is simply the blockage of large particles by small holes, 2) <u>Physio-chemical attraction</u> which involves the tendency of oxide particles to cluster and attach themselves to each other and the filter spines, 3) <u>Tundish flotation enhancement</u> which results from the decrease in molten metal turbulence in the pouring vessel and 4) <u>Hydrodynamic separation</u> by which particles are trapped in eddies within the torturous filter channels. Previous literature strongly suggests that the primary mechanism for filtration is the physio-chemical removal. Filtering efficiency relationships such as presented by Apelian[3]

$$\eta = \frac{C_i - C_o}{C_i} = 1 - \exp\left[\frac{-K_o L}{U_m}\right] \quad (3)$$

where:

η = the effiency

C_i = conc. before filtration

C_o = conc. after filtration

U_m = melt approach velocity

K_o = kinetic parameter

L = length of filter

imply that the ability for physio-chemical attraction to occur is a function of the time the oxide particles are in close vicinity of the filter material. The evidence gathered in the present study suggest that this mechanism may not be the primary cause of oxide removal.

If physio-chemical attraction was the primary cause for oxide removal, one would expect to find large residual particles in the filter cross sections. Cross sectioned filters from pour cup assemblies, after casting, contained metal solidified in the cavities and on top of the filters. In Figure 4, the SEM image and elemental maps illustrate the typical oxide film observed at the interface between the metal and filter spines. In filters from standard and rhenium modified U-700B, Al_2O_3-MgO spinel material was found in the interface film. At the pour temperature used in this experiment (1650°C), MgO used to stabilize the zirconia, may be reduced to form the more stable Al_2O_3 from elemental aluminum in the melt due to the differences in oxide stability as indicated by the Relative Free Energy of Formation of the oxides at pour temperature, Table II. In the filters used in the hafnium modified and the yttrium modified alloys, hafnia and yttria respectively were found at the interfaces. Hafnium and yttrium form more stable oxides and can reduce the ZrO_2 or the MgO from the filter material. No evidence of particle adhesion was observed at the metal/filter interfaces. The width of the films observed at the filter interface were in the order of 1-2μm which were smaller than the particles eliminated from the rafts of the filtered material. The oxide film from the filter spines of the yttrium modified alloys was yttria, yet the particles eliminated from the rafts of the filtered samples of this alloy were alumina.

Table II   Relative Free Energy of Formation for oxides of interest at pour temperature, 1650°C.

OXIDE	$\Delta F°$ (Kcal)
2 MgO	-162.6
2/3 Al_2O_3	-170.3
ZrO_2	-175.4
HfO_2	-180.6
2/3 Y_2O_3	-202.4

Figure 5 shows that large and small particles of oxides including Al_2O_3 were found in the layer of metal frozen on top of the filters. Surface tension of the liquid metal prevents this material from passing through the filter at the end of the pour and it therefore solidifies at the top of the filter disk. The size and chemistry of these particles are similar to those of the type of particles missing from the raft of the filtered melts and is a result of flotation during pouring. The flotation of these particles is improved by the change in flow within the pour cup when the filter is present. The observation of this phenomena suggests that this flotation enhancement plays a major role in the separation of particles from the pour stream. It may result from a combination of factors including a more constant metal head in the pour cup and reduced turbulence at the bottom of the cup.

While oxide flotation was previously considered a supplementary effect of filtration, it appears that filters are very valuable in controlling turbulence that keeps fine oxides in suspension. If this observation is correct, the filtering efficiencies predicted by equation (3) are still valid, since the same factors which promote physio-chemical attraction (low melt velocities and thick filter thickness) also increase the ability for oxide particles to float out in the tundish.

A 125mm³ sample was taken from each alloy for melting in a sessile drop furnace using a substrate made from the same material as the filters (Figure 6). The alloy samples along with the ceramic substrates were
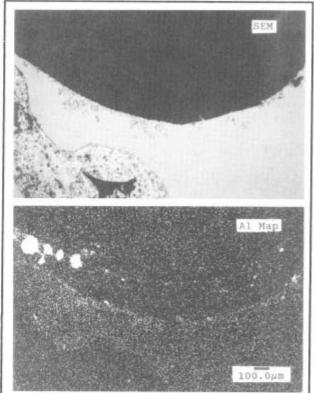

Figure 5. SEM photo and elemental maps showing oxide particles at top of filter.

heated in vacuum to a temperature of 167°C (300°F) above the liquidus. The metal droplet and the substrate interfaces were
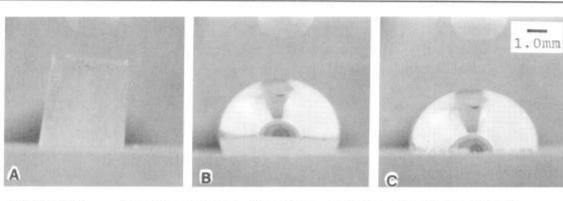

Figure 6. Three photos showing stages of the sessile. Zirconia substrate is at the bottom, metal specimen is placed on the substrate, and the object at the top of photo is the thermocouple. (A) Before melting (B) At melting (C) Metal reaction with substrate

examined in the SEM. Figure 7 shows a typical film found on the interface of the metal sessile drop and its substrate and these films are similar to those found on the filter interfaces. For the samples of the standard and rhenium modified alloy a film of Al_2O_3+MgO was observed. The interface of hafnium modified alloy drop contained a film of HfO_2 and the interface of the yttrium modified alloy drop contained a film of Y_2O_3. The widths of these interfaces were 5-10μm. The oxide products found at these interfaces are from reactions between the MgO stabilized ZrO_2 substrates and the stable oxide formers in the
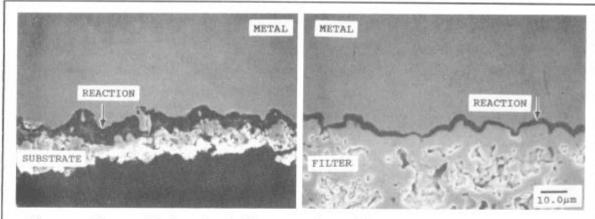
Figure 7. Interfacial reaction films found in both the sessile drop specimens and the filter after pour. (U-700B)

molten alloy. This supports the hypothesis that the films found on the filter interfaces are formed by reactions between the filter material and the molten alloy during pouring.

Conclusions

- Thin oxide films are formed on the filter spines during pouring.

- The minor addition of the elements hafnium or yttrium enhance the cleanliness of the melt by reducing Al_2O_3 inclusions. While the unfiltered Re modified alloy appeared cleaner, this was judged to be due to a sampling problem.

- Filtration of U-700B with minor additions of hafnium or yttrium significantly reduces the amount of Al_2O_3 found in the melts.

- No particles were found adhering to filter spines in any of the poured filters. Large and small particles of Al_2O_3 were observed at the top layer of the metal in the filter cross sections. Small particles were found in the metal solidified between filter spines but no particles were found in the filter-metal interfaces.

- Particle adhesion or physio-chemical attraction does not appear to play a major role in the reduction of oxide particles. The major proportion of the oxide reduction is due to enhanced flotation of oxides above the filter.

Recommendations

- The further study of the effects of other minor elements and the definition of minimum concentration for effective filtration may introduce the development of cleansing elements for ultra-clean superalloys.

- The study of tundish design is recommended to take advantage of the flotation improvement benefits achieved by the use of filters in pour systems.

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