RECYCLING OF ENGINE SERVICED SUPERALLOYS

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ABSTRACT

With the increasing shortages of critical raw materials for high temperature alloys, recycling of scrap is mandatory.

However, because of the likelihood of picking up contaminants such as S, O, Pb, Na and Cl from combustion products and protective coatings on the original blades, parts which had seen engine service cannot be recycled directly by vacuum induction melting.

These scrap materials are, therefore, sold to the smelters at prices far below their intrinsic elemental value by today's market.

A unique recycling system is in use whereby contaminated scrap, as well as entire engines, are segregated into pedigreed alloy lots, then melted in an electric arc furnace with oxygen lancing. This oxidizes all the reactive elements such as Al, Ti, Zr and Hf and purges any low melting elements.

This "stripped" alloy is then fully analyzed for residuals and the chemistry is fed into a computer with a least-costing program to calculate corrective additions necessary.

The material is reconstituted by vacuum induction melting and is refined back into usable superalloys. The result is a product meeting all specification requirements at a cost far lower than either all scrap or virgin heats.

The overall outcome is that critical materials such as: Co, Mo, Ta, W, etc., are preserved and the dependence on imported materials is significantly reduced.

The paper will detail the melting procedures with typical analyses for alloys such as PWA 1455, and comparisons with conventionally cast nickel and cobalt base superalloys.

Introduction

In the last few years, we have seen dramatic changes in the price and availability of a number of raw materials that are crucial in the performance of gas turbine engines and other high temperature applications.

Elements such as cobalt, molybdenum, tantalum, columbium, etc., have caused availability problems on the world's metal markets and a rapid search for substitutes and replacements by the turbine engine builders has been initiated.

The shortages have forced alloy suppliers to study alternate sources of elements and institute recycling and reclamation programs.

Because of the danger of undesireable materials getting used in these premium quality alloys, protection of the system by pedigreed manufacturing processes and tight controls have limited the use of large amounts of available scrap, which can then only be used in non-critical applications.

In doing so, the intrinsic value of the material is often reduced to very low levels, with resulting financial loss as well as a greater reliance on imports, since the scrap cannot be recycled into premium superalloys.

One such area is the use of engine-serviced hardware, where parts that have been running for a considerable time need to be replaced when they fail. These scrap parts cannot often be directly remelted into ingot since they are oxidized, they have combustion products entrained in the surface and maybe residual coatings.

Much of this contamination would not be removed by vacuum induction melting, even with pre-cleaning of the parts and hence this scrap is smelted down for its contained nickel content, with the result that the other expensive alloying elements lose their value.

The intent of this program was to take this low value scrap and by various refining processes, remove any harmful products, reclaim the usable critical elements and produce premium quality superalloy once more.

The Program

The basic concept of this program was to acquire scrap PWA 663 (B1900) and PWA 1455 (B1900+Hf), sort, charge into an arc furnace, oxygen lance to oxidize any reactive elements, the resulting product would then be further refined by vacuum induction melting.

1. Raw Materials

8,500 pounds of scrap blades and vanes were acquired that had been stripped from engines during regular maintenance checks. Because of the likelihood of mixing with blades of other compositions, the parts were sorted by a portable field spectrometer to identify the B1900+Hf.

Many of the parts were severely corroded and oxidized, others were fractured and had combustion products adhering to the surface.

Random samples were taken and a full chemical analysis run on the clean metal. The nominal chemical analysis of the alloy is shown in Figure 1.

Figure 1

CHEMICAL ANALYSES

B1900+Hf

Element	PWA 1455 Spec.	Scrap Analysis (Aver.)	Arc Ingot	Vacuum Melted Ingot
C	0.08-0.13	0.08	0.10	0.11
S	0.015x	0.001	<.001	0.002
Fe	0.35x	0.12	0.53	0.33
Mo	5.75-6.25	5.92	5.67	5.95
Cb	0.10x	0.02	0.12	0.08
Ti	0.8 -1.2	1.05	0.80	0.98
Cr	7.5 -8.5	7.95	9.31	7.68
Co	9.5-10.5	9.74	10.31	9.87
Ta	4.0 -4.5	4.09	3.80	4.20
Zr	0.13x	0.049	0.022	0.030
Mn	0.20x	0.02	0.08	0.05
Si	0.25x	0.03	0.35	0.23
Al	5.75-6.25	6.15	1.21	5.92
B	0.01-0.02	0.013	0.017	0.015
Hf	1.05-1.25	1.17	<.01	1.25
O	--	25 ppm	14 ppm	3 ppm
N	--	23 ppm	85 ppm	14 ppm

2. Arc Refining

The 8,500 pounds were charged into a basic 3-phase direct arc furnace with magnesite hearth and walls which had previously melted several nickel base heats so as to minimize iron pickup from the normal ferrous production alloys. A lime and fluorspar slag was introduced to minimize volatilization of critical elements and to complex the oxidizable elements. When the bath was molten, approximately at 2900°F (1600°C), a sample was taken to check the start chemistry and to monitor the subsequent refining. Figures 2 and 3

Figure 2

MAJOR ELEMENT CHANGES IN ARC REFINED B1900+Hf

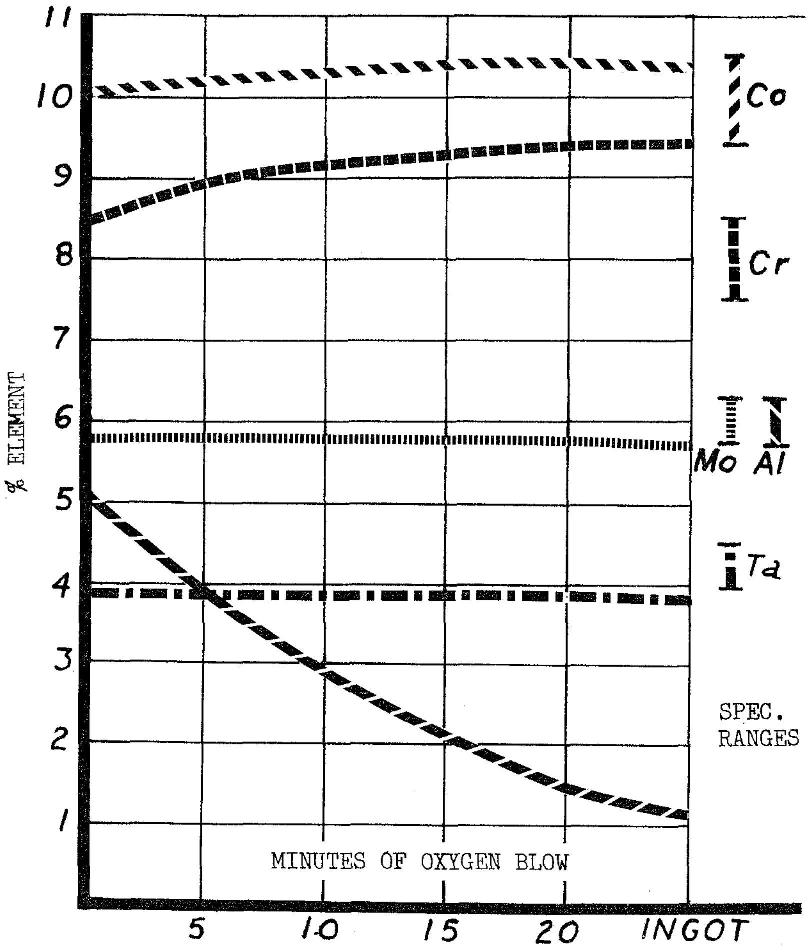
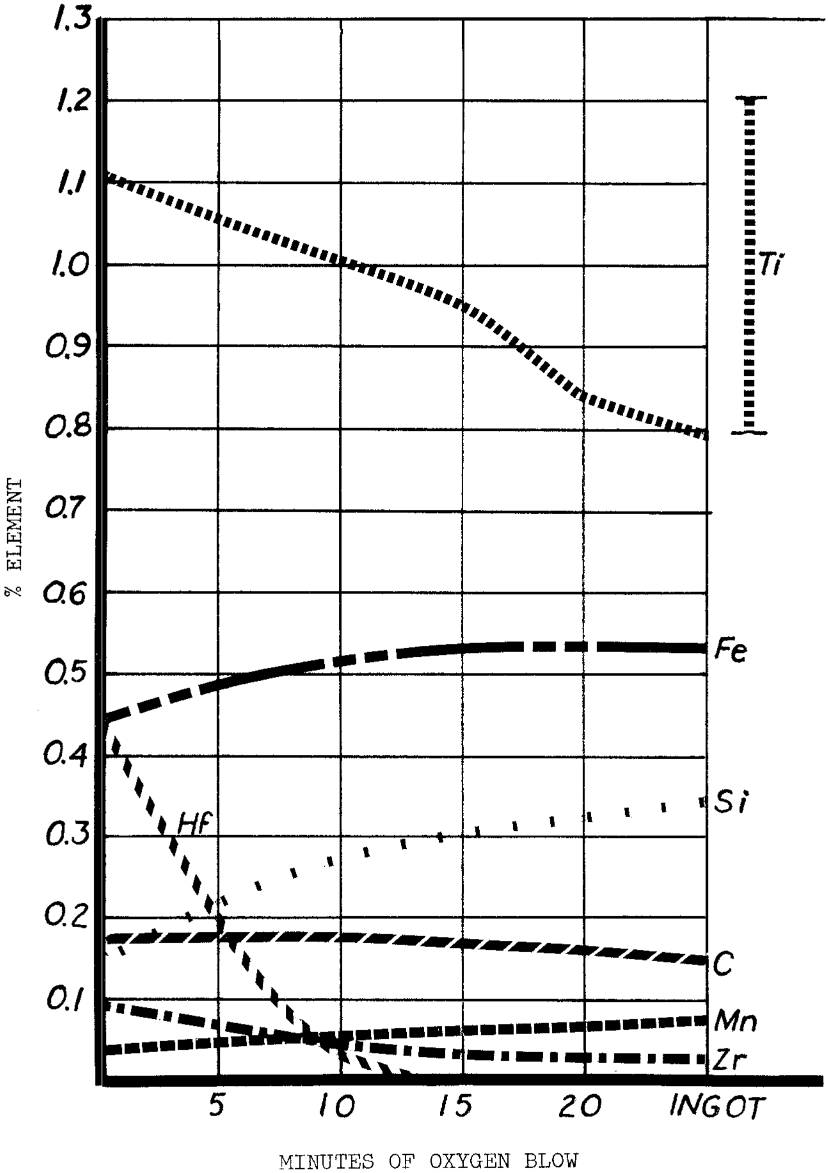


Figure 3

MINOR ELEMENT CHANGES IN ARC REFINED B1900+Hf



A pure nickel lance (also to prevent iron pickup) was plunged into the bath and oxygen was blown for 5 minutes and a sample was taken for chemistry check (Figures 2 and 3). This process was repeated three more times with 5 minute oxygen blows and chemistry checks until most of the reactives were removed.

Figures 2 and 3 show the chemistry checks of the major and minor elements after each of the oxygen treatments, graphically depicting the effect on the various elements present.

The elements that were reduced significantly were Al (6.0%→1.5%), Ti (1.1%→0.8%), Hf (1.1%→zero), and Zr (0.1%→0.02%). As a result of their removal, there was an enrichment of Cr (8%-9.4%), Co (9.7-10.3) and little change in Mo and Ta.

There was a pickup in Si and Fe due to processing, as well as O and N. After 20 minutes total time of oxygen lancing, approximately 6% of the overall 8% of contained reactives had been removed, so it was decided to pour the heat since further processing could start to oxidize the critical elements.

The heat was tapped into a ladle and the first half of the heat was poured into cast iron permanent pig molds, the rest via a pigging machine into 25 pound ingots.

The total weight of ingots produced was 7,909 pounds, or a yield of 93%. Since the reactive loss was about 6%, this meant that there was an almost complete recovery of the non-reactive elements.

Ingots representing the first, middle and last portion of the heat were analyzed, but other than a decrease in oxygen content, there were no substantial differences in chemistry. The final oxygen content of the bath was 183ppm and the 3 ingots were 42ppm, 14ppm, and 12ppm respectively.

This decrease in oxygen was probably due to flotation of oxides that had been suspended within the melt during the vigorous agitation of the bath. Atomic absorption and mass spectroscopy of the ingots did not reveal any undesireable elements, also, no yttrium was found, which could have been present from coatings. (Figure 4)

Figure 4

TRACE ELEMENT ANALYSIS

OF ARC REFINED B1900+Hf

Values in PPM

By Mass Spectroscopy

Th	<0.22	Cd	<1.0	Zn	0.89	Na	<.10
Ba	<0.10	As	3.9	V	40	Y	<.10
Sb	<0.47	Ge	0.13	Ca	56	La	<.10
Sn	<1.6	Ga	8.9	K	0.02		

	Mass Spec.	Atomic Absorption
Pb	0.27	1.0
Bi	<0.10	<0.10
Se	0.10	<0.10
Te	<0.10	<0.10
Tl	<0.10	<0.10
Ag	<0.24	0.13
Mg	>1600	300 ppm

Samples of the slag were also analyzed and the values are shown in Figure 5. It can be seen that the Al and Ti from the alloy have gone into the slag, and there is a decrease in the Cr content, consistent with the increase in the alloy.

Figure 5

ANALYSIS OF SLAG

ON ARC REFINED B1900+Hf

	Before Lancing	After Lancing
Al_2O_3	5.1%	10.4%
Ca O	10.2%	10.2%
$Si\ O_2$	76.5%	30.8%
MgO	11.6	23.7%
Cr_2O_3	13.5%	4.4%
F	1.0	2.0
$Ti\ O_2$	<0.5%	5.0%

3. Vacuum Refining

Because of the pickup of Fe and Si, it was decided to dilute them by realloying on a 50/50 basis with virgin material. (Figure 6)

Figure 6

VACUUM HEAT CHARGE

Arc Ingots = 2850 lbs.
Virgin + Adds = 2879 lbs.

Total Charge = 5729 lbs.

	Virgin %		Arc Ingot %		Theoretical %	Actual %
Co	4.68	+	5.16	=	9.84	9.87
Cr	3.18	+	4.65	=	7.83	7.68
Mo	3.05	+	2.83	=	5.88	5.95
Al	5.36	+	0.60	=	5.96	5.92
Ti	0.61	+	0.40	=	1.01	0.98
C	0.05	+	0.05	=	0.10	0.11
Hf	1.19	+	-	=	1.19	1.20
Ta	2.44	+	1.90	=	4.34	4.20
Ni	29.67	+	Bal.	=	Bal.	Bal.

The base charge of elemental Ni, Co, Cr, Mo and Ta was refined in a 6,000 pound Inductotherm vacuum induction furnace and the arc processed material charged in. After a second refine, the reactive elements Al, Ti and Hf were added, the entire melt refined and poured off into ingots. When the arc ingots were melted, no outgassing was observed and the entire melt appeared very clean and free from slag and dross.

The analysis of this 50/50 heat is shown in Figure 1. Full trace element analysis was run, also a microcleanliness evaluation performed on the first, middle and last ingots poured. The alloy complied with the industry specification and was submitted for castability studies.

4. Casting Evaluation

Production investment castings of turbine blades were poured from the alloy and X-ray and zyglo yields compared with standard alloy. Test bars were cut from the castings and tensile and stress rupture tests were performed, per the specification requirements. In all tests, the alloy was judged from good to above average when compared to conventionally produced B1900+Hf.

As a result of the extensive testing, the entire refining process has been approved and is now in continuous production.

Economic Considerations

Other than the technical viability of this alloy production program, the economic aspects were the primary motivators in designing the process.

At the time that the pilot program was started, Ta was around $170 per pound, Co $25 per pound, and Mo $30 per pound, and the cost of a virgin heat of B1900+Hf was around $20 per pound.

This 50/50 heat, with all the processing involved was valued at around $13.00/LB., a net saving of around $7.00 per LB, or 35%. Increasing the percentage of the recycled material would effect even greater savings and with subsequent improvements in scrap segregation and processing, reductions of over 70% over the virgin cost have been realized.

Other alloy systems have shown similar dramatic cost reductions when scrap has been processed and refined using this technique. The minor impact of increased manufacturing costs and handling is greatly outweighed by the overall reduction in raw material costs.

Discussion

The process of arc melting scrap material is not new, but nickel base superalloys have rarely been melted on their own, usually they are mixed with ferrous scrap for their contained nickel content to produce low alloy and stainless steels.

The reactive elements such as Al, Ti, Zr, Hf, etc., cause dross problems when melted in air induction furnaces, hence this technique could not be used for reclamation. The presence of surface contamination and the chance of trace element pick up, precluded the use of engine serviced blades and vanes from being vacuum melted directly.

The unique concept of tandem melting in arc and vacuum, however, does open up a new field in critical materials recycling and recovery.

The arc refined material can also be used as a partial ingredient in other nickel base alloys other than B1900+Hf. For example, it can be used in the charge formulation of Mar-M alloy 246, Mar-M alloy 247, In 792 and In 738. In doing so, it can ease the demand for Ta, Mo and Co in these alloys at considerable cost savings. Figure 7 shows the amount of arc refined B1900+Hf that could be utilized in these alloys and the reduction in cost that can be realized.

Figure 7

ARC REFINED 1455 SCRAP

IN OTHER ALLOYS

Alloy	% Arc Refined Scrap	Cost Savings Over 100% Virgin
Mar-M alloy 247	12%	6%
IN 738	31%	21%
IN 792+Hf	35%	17%
Mar-M alloy 246	44%	25%

Apart from the direct refinement of specific alloys, mixtures of alloys or joined pieces can also be reclaimed. For example, entire gas turbine engines have been acquired as scrap, and stripped down into various components. This rough separation of burner cases, blades, vanes, shafts, etc., can separate alloys into various classes which can be accumulated until a sufficient volume for arc reclamation is reached.

Other sources of critical elements can include grinding and cut off dust from finishing operations, sludges from electroprocessing, weldments and machining turnings.

These various scraps are charged into the arc furnace and oxygen lanced as described. The resulting ingots are analyzed and the chemistry obtained is fed into a computer which has the capability to determine which alloys can be produced from that chemistry and the percentage required.

This consolidation of variegated lots can produce alloys whose chemical composition bears no resemblance to any known alloy, but whose separate constituents can be maximized within a particular charge to decrease virgin material usage.

Moreover, separate lots from several arc reclaimed heats can be blended together to further increase the usage of scrap since they can be vacuum refined together, and produce a desired alloy within certain specifications.

With further arc processing refinements, it should be possible to charge the entire product of the arc furnace into the vacuum induction furnace, refine, and add back only the reactive elements lost in the arc furnace.

Conclusions

Because of the expanding market in gas turbine engines, the demand for high temperature superalloys has greatly increased in the last few years.

Greater demands for reliability and property improvements have dictated the use of alloys containing elements that are either scarce or in geopolitical areas of unrest, resulting in severe shortages and rapidly escalating prices.

As in any other materials systems, the role of scrap is important since by recycling, the need for new materials is decreased. However, with the premium quality superalloys, the concern for contamination with undesireable elements and the need for traceability has caused a large source of scrap to be eliminated as recyclable back into superalloys. This source is engine-serviced hardware which, because of the lack of demand, is sold off as scrap on the world's market and melted as nickel units into steel.

The other elements such as cobalt, tantalum, tungsten, etc., are thus lost and have to be replaced by imported virgin materials for the production of superalloys.

This program has successfully demonstrated that engine-serviced blades and vanes, as well as other non-pedigreed sources of scrap, can be readily reclaimed and refined, and produced as premium quality superalloys, with no contamination problems. The critical elements are fully recovered and recycled with minimum losses and this results in dramatic cost savings, with a concommittant decrease reliance on imports.