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PLASMA ARC MELTING OF ZIRCONIUM

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PLASMA ARC MELTING OF ZIRCONIUM

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ABSTRACT

Zirconium, like some other refractory metals, has an undesirable sensitivity to interstitials such as oxygen. Traditionally, zirconium is processed by electron beam melting to maintain minimum interstitial contamination. Electron beam melted zirconium, however, does not respond positively to mechanical processing due to its large grain size. We undertook a study to determine if plasma arc melting (PAM) technology could be utilized to maintain low interstitial concentrations and improve the response of zirconium to subsequent mechanical processing. The PAM process enabled us to control and maintain low interstitial levels of oxygen and carbon, produce a more favorable grain structure, and with supplementary off-gassing, improve the response to mechanical forming.

INTRODUCTION

Traditionally, electron beam melting has been used for initial zirconium melt processing. This technique helps control the amounts of gettered contaminants such as oxygen and carbon. The disadvantage of our electron beam-melted zirconium was the large grain size that contributed to difficulties in further mechanical processing.

In general, plasma arc melting has the benefit of operating under a wide range of pressures (from vacuum to greater than atmospheric), varying the plasma feed gases, and producing finer grain structures. By the addition of reactive gases to the plasma stream, melt pool chemistry can be refined and modified to control the amounts of metallic and interstitial contaminants. Hydrogen is the obvious choice for a reactive plasma gas due to its high thermal conductivity, its affinity for combining with melt contaminants, and its relatively low cost. Mimura et al.^[1] have shown the benefits of PAM with hydrogen in the removal of contaminant alloying elements from scrap zircaloy. Their study used small amount of zircaloy (13 grams) and relatively long melt times (300 minutes). We were interested in much larger quantities and feed rates. Dunn et al.^[2] have shown the control of interstitials in much larger melt masses of tantalum (several kilos) and much shorter gas-metal interaction times. In this work the effect of shorter interaction time in zirconium is being studied.

Treco^[3] has shown in zirconium a correlation between increased oxygen concentration and both increased hardness and tensile strength and decreased ductility. We used hydrogen in our plasma stream to maintain or reduce the oxygen and carbon concentrations and minimize their embrittling effects. In this study, we used hardness as the measure of contaminant control. By returning the hardness of the melted material back to that of the starting crystal bar, we have kept the interstitial contamination low, and refined the grain structure to be more suitable for further mechanical processing.

EXPERIMENTAL DETAILS

This work was conducted in a Retech 150kW single-gun plasma arc melter (schematic - Figure 1). The melt chamber is evacuated to approximately 50 μm Hg, back-filled with argon, purged, then back-filled with argon again. Material is fed in from the side above the 4 inch (10cm) diameter water-cooled copper crucible. The torch is manipulated by computer to melt and drip some of the feed stock into the melt pool contained in the crucible. The ingot can be withdrawn down through the crucible by hydraulic ram.

Figure 1 - Plasma Arc Melter Schematic

When an appropriate amount of material (≈ 1 inch pool depth) has been fed to the melt pool, the feed material is withdrawn and the torch pattern reset to work on the melt pool. The ingot can be withdrawn down through the crucible by hydraulic ram. Up to four separate feed gases can be mixed and used as the plasma medium. In this work we used a combination of ultra high purity argon and helium-6%hydrogen mixed in roughly a 25% Ar and 75% He-6H mixture.

Two separate melts were performed for this experiment. After melting, hardness and metallography samples were taken from the ingots. Additional samples were vacuum annealed to remove the hydrogen from the zirconium. Hardnesses were taken of the starting crystal bar as well as the melted material before and after heat treatment to determine the levels of impurities. Chemistry samples were not taken.

RESULTS and DISCUSSION

Zirconium Melt 1

For the first melt, the plasma torch feed material was formed from six 15mm diameter zirconium crystal bars (≈ 7 kg total mass) bundled together with pure zirconium wire. The melt chamber was initially evacuated to 30 μ m Hg then back-filled with argon. Feed gas was supplied at a pressure of 45psi (310kPa) and a flow rate of 2.5 cfm (70.8 liters per minute). The gases were mixed approximately 1:4 with 0.6 cfm (17 lpm) argon and 1.9 cfm (53.8 lpm) He-6H making an effective hydrogen concentration in the feed gas 4.56%.

The crucible withdraw mechanism failed early in the run and the melt had to be stopped after five minutes of melting. Even so, the zirconium melted quite easily and quickly. Approximately one-third (2.2 kg) of the feed material was melted. The ingot was halved axially and a 100g sample was taken along the center line of the ingot. Half of this sample was prepared and submitted for hardness testing. The other half was annealed at 800°C (1472°F) for one hour. After annealing, this sample was also tested for hardness. The results of the hardness tests are shown in Table 1.

Table 1
Vickers hardness results from zirconium plasma melt #1
(5kg load, 15 second dwell)

	HV	HRB
Initial zirconium crystal bar	70.8	<< 40
Zirconium after plasma melting #1	105.3	55
Zirconium after heat treating	73.1	<< 40

Conversion to Rockwell B from Houk^[4]

As shown in the table above, the hardness increased after exposure to hydrogen during melting and decreased after subsequent heat treatment. Conversions were made from Diamond Pyramid Hardness scale to Rockwell B for comparison. Rockwell B hardnesses for zirconium are not reported for values less than 40 (HV 90). The final hardness after heat treatment clearly is back to the hardness seen in the original crystal bar. This appears to confirm our hypothesis that plasma arc melting can maintain the amount of interstitial oxygen by replacing potential host sites with hydrogen in the feed gas. The embrittlement caused by the hydrogen is then removed by heat treatment.

Zirconium Melt 2

As with the first melt, the plasma torch feed material for the second melt was formed from six 15mm diameter zirconium crystal bars (≈ 6.5 kg total mass) bundled together. In this case the bars were 'welded' together in a non-consumable electrode arc melter before being loaded into the plasma melter. This was to help alleviate some difficulties with the feed mechanism during the first melt. The chamber was evacuated to 80 μ m Hg then back-filled with argon. Feed gas was supplied at a pressure of 45psi (310kPa) and a flow rate of 2.5 cfm (70.8 lpm). The gas mixture was identical to Melt 1.

During this melt, there were few mechanical difficulties and the majority of the zirconium (≈ 5.5 kg) was melted. Approximately 0.5" (12.7mm) of the outer diameter and ends of the ingot were

machined off to leave a 3 inch (76mm) diameter slug 3.5 inches (89mm) long. A 0.25" (6.3mm) slice was taken off the end of the ingot and the slice halved to form two semicircles. Hardnesses were taken across the faces of both the ingot and both slices. The ingot and one slice were vacuum annealed at 800°C (1472°F) for 100 hours. Hardnesses were taken of the heat-treated ingot and slice. This hardness data as well as hardnesses taken from the electron-beam melted zirconium are shown in Table 2. The results are similar to plasma melt #1 in that the hardness increases after plasma melting but decreases to initial levels after heat treatment.

Table 2
Rockwell hardness results from zirconium plasma melt #2
(0.0625" (1.6mm) ball, 100 lb. (45.5kg) load)

	<u>HRF</u>	<u>HRB</u>	<u>Std Dev</u>
Zirconium after electron beam melting	44	---	6.3
'Welded' zirconium crystal bar	---	45.1	8.5
Zirconium after plasma melting #2	92.1	66.1	3.1
Zirconium after annealing	86	51.1	10.4

In comparison to the first melt, the hardness numbers in the second melt were significantly higher. This can be attributed to the 'welding' performed on the initial crystal bar. In additional melt tests, we found that processing zirconium in our non-consumable electrode arc melter caused hardnesses to increase dramatically, in one case hardnesses of HRB 85 were seen. We believe that during this pre-processing step, additional oxygen was gettered by the zirconium causing increased initial hardness. Even though the two melts differ in hardness values, it is clear that the plasma arc melting technique with subsequent heat treatment is an effective method to maintain interstitial oxygen contamination at low levels.

The end surfaces of both the plasma arc melted zirconium (Figure 2) and the electron-beam melted zirconium (Figure 3) were polished and etched. Each of the ingots are 3 inches (76mm) in diameter and 3.5 inches (89mm) long. As can be seen in the Table 3 and the following photo macrographs, the average grain size in the plasma melted material is approximately one-third that of the electron-beam melted material. There is also a greater than ten fold difference between the diameters of the finest plasma melted grains and the coarsest electron-beam melted grains.

Table 2 shows a significant difference in hardness between the electron beam melted zirconium and the plasma melted zirconium. Two factors certainly lead to this result. First, as previously stated, the initial feed material for PAM melt #2 had a significantly higher hardness due to pre-processing. We do not have any characterization of the feed material used in the electron beam melter. It is quite possible that the electron beam melted ingot was processed from crystal bar of lower oxygen concentration than in either of the two plasma melts. In addition, hardnesses will tend to increase with grain refinement. Since the plasma melted ingot has a much finer grain structure, we would expect the hardnesses to be elevated when compared to the coarser grained material.

Table 3
Average Grain Size Measurement

	Average Grain Size	
	ASTM Macro-Grain Size Number	'Diameter' of Average Grain Section
Plasma melted zirconium	M-6	0.18" (4.5mm)
Electron-beam melted zirconium	M-3	0.5" (13mm)

Figure 2 - Plasma arc melted Zr

Figure 3 - Electron-beam melted Zr

CONCLUSION

Based on hardness data, plasma arc melting provides an excellent alternative to electron beam melting for the processing of zirconium. Plasma melting offers the benefit of decreased grain size while maintaining the interstitial oxygen contamination at initial levels. Future development work on this topic include detailed chemistry analysis, parameter studies on the melting and heat treating, and response to mechanical forming.

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