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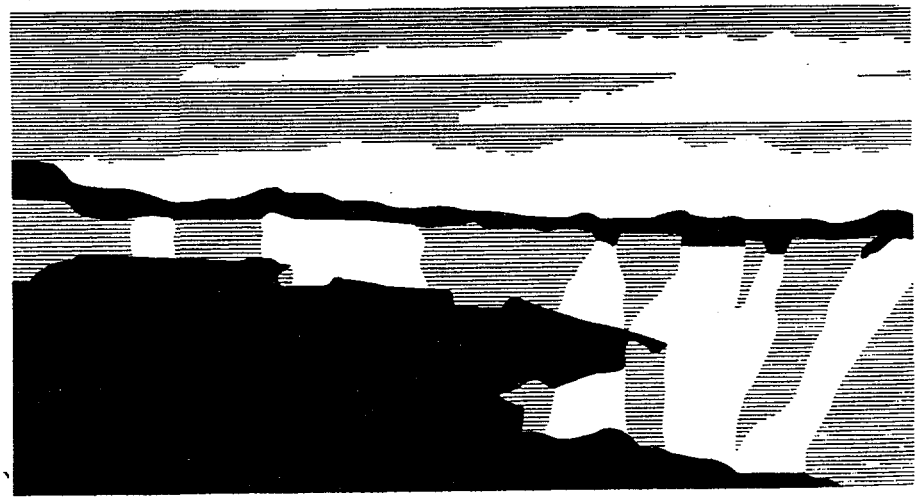

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CHEMISTRY MODIFICATION OF HIGH OXYGEN-CARBON POWDER BY PLASMA MELTING

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Abstract

State-of-the-art melting of tantalum and tantalum alloys has relied on electron beam(EB) or vacuum-arc remelting(VAR) for commercial ingot production. The limited number of melting techniques for these materials are the result of the high melting temperatures and reactivity with conventional mold/crucible materials. In addition, the required vacuum levels used in the EB and VAR processes, limit these techniques to relatively low interstitial content material due to extensive outgassing during melting.

Plasma arc melting(PAM) provides an alternative for melting tantalum and offers the advantage of processing under inert or other gases rather than vacuum. The plasma process is not sensitive to material outgassing and allows for the direct recycling of material that would otherwise be reprocessed by chemical extraction. The current work examines melting of high interstitial content tantalum powder by the plasma arc process. Various cover gases of argon-hydrogen and helium-hydrogen were investigated to determine best melt quality. Melted ingots were characterized by chemical and metallographic methods to determine overall interstitial content, compound and morphology.

Introduction

Commercial production of tantalum and tantalum alloys have historically used EB or VAR processes as the preferred melting method. The limit on melting techniques is due to the high melting temperature and reactivity of tantalum. Both melting techniques produce quality material because of the vacuum atmosphere inherent to the process. The relatively high vacuum during melting promotes the volatilization of interstitials such as carbon and oxygen which results in final overall levels on the order of 50 ppm or less. In addition to interstitials, the EB and VAR processes also promote the vaporization of other metal impurities such as iron and copper and provided a refining method for the production of high purity material(1). As with any technique, the EB and VAR processes have limits on the form and purity of material that can be processed. For instance, the VAR process requires structural integrity and electrical conductivity of the starting material in order to fabricate an electrode. In addition, the fabricated electrode must be of similar cross section over the length if the arc is to be controlled. The EB process requires a constant vacuum for the electron guns to function which limits the amount of outgassing that can occur during melting. However, material form is not a concern due to the side feed or hearth configuration of most EB systems.

The plasma arc melting(PAM) process offers the unique advantages of both EB and VAR. Starting material is side fed as with EB so that starting feed form is not a concern. However, the PAM process operates under inert atmospheres, so that outgassing of feed material does not disrupt the melting process. The gas from the melt is simply swept out of the melt chamber. The plasma melt process also allows flexibility in plasma gas composition which relates to significant changes in melt quality and chemistry during melting. For example, the plasma process allows melt chemistry modification by injecting various gas elements; hydrogen, oxygen, carbon dioxide or nitrogen into the cover gas which react with the melt to reduce oxides, remove carbon through the formation of carbon monoxide, or form nitrides in the melt.

Previous work by Minura and Nanjo(2) has demonstrated that tantalum oxide can be reduced with plasma as the heat source by the carbothermal reduction process. This work concentrated on variations in carbon-oxygen ratios in the starting material, and studied the affect of argon-hydrogen gas mixtures on final button chemistry. The experimental samples were very small; 7 grams, and the melt rates very low, 1 gram/min, compared to commercial practices. The purpose of this work was to 1) evaluate the plasma arc melting process for the recycle of very low grade tantalum powder containing excessive levels of interstitials, 2) determine the effect of argon-hydrogen and helium-hydrogen plasma gas mixtures on melt quality and final interstitial content, and 3) establish a processing window to determine the trade-offs between plasma cover gas and melt rates.

Plasma Thermodynamics

Melt Quality/Efficiency

The temperatures associated plasma melting can result in thermodynamic equilibria not commonly found in other melting processes. The variation in gas thermophysical properties and gas/metal thermodynamics effect the melt quality as well as the chemical interaction between plasma gas and the melt. Plasma torches are typically operated with a helium-argon mixture with plasma gas temperatures ranging from 5000-10000 C (3). At these temperatures, a plasma gas consisting of helium-argon will contain these elements in non-ionized form. However, the addition of hydrogen to the gas dissociates the diatomic hydrogen to monatomic hydrogen and potentially ionized hydrogen(4). Figure 1 shows the variation in heat content and dissociation temperatures of various gases as a function of gas temperature.

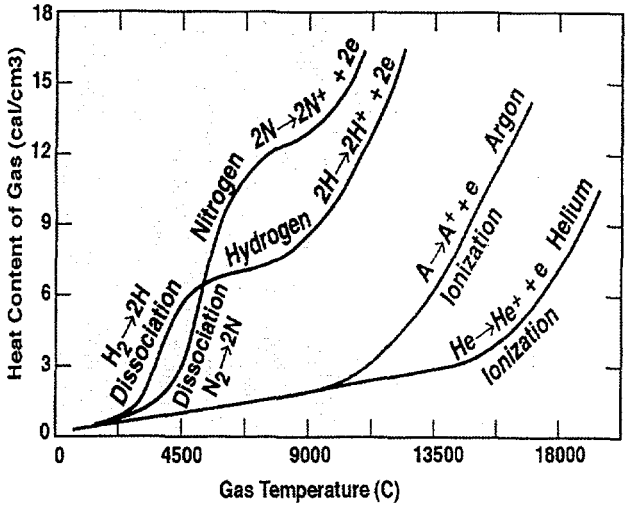


Figure 1: Heat Content of Various Gases as a Function of Temperature(4).

From the melting perspective, monatomic hydrogen results in a ten fold increase in gas heat energy compared to argon or helium. The large increase in heat content will promote improved melting at any set of constant melting parameters. While the plasma process may result in ionized hydrogen, the short recombination times for this species(5) does not allow for any energy contribution in these melting systems. Similarly, the thermal conductivity of different gases will also vary melt quality. Figure 2 shows the variation in thermal conductivity of different plasma gases as a function of temperature(6). Over the temperature range of interest, helium and hydrogen will be more efficient plasma gases for melting compared to argon.

Melt Chemistry

The chemical reactions in the melt using typical inert plasma gasses, helium and argon, are the same as with EB and VAR. Specifically, oxygen/carbon reduction by the carbothermal reaction or direct oxygen reduction by volatilization. However, the ability to inject reactive gas species into the plasma system allows other atypical chemical reactions to be considered during the melting process.

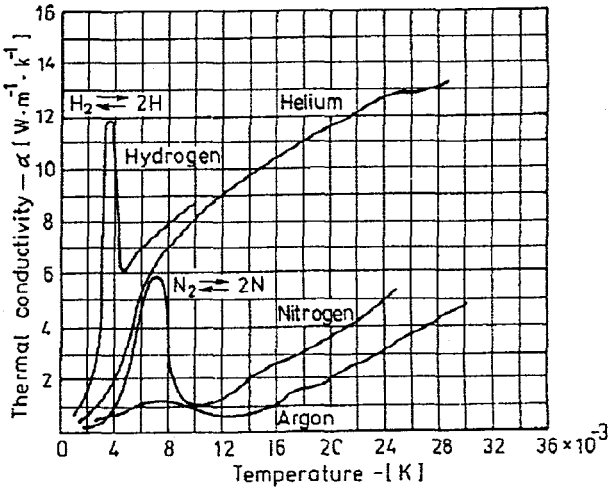


Figure 2: Thermal Conductivity of Plasma Gases6)

Recent work by Robino(7), Figure 3, shows the increased negative free energy of formation with oxygen using monatomic hydrogen compared to the standard diatomic species. The calculations are plotted on a standard Ellingham-Richardson Diagram(8,9) to show the effectiveness in reducing many different metal oxides.

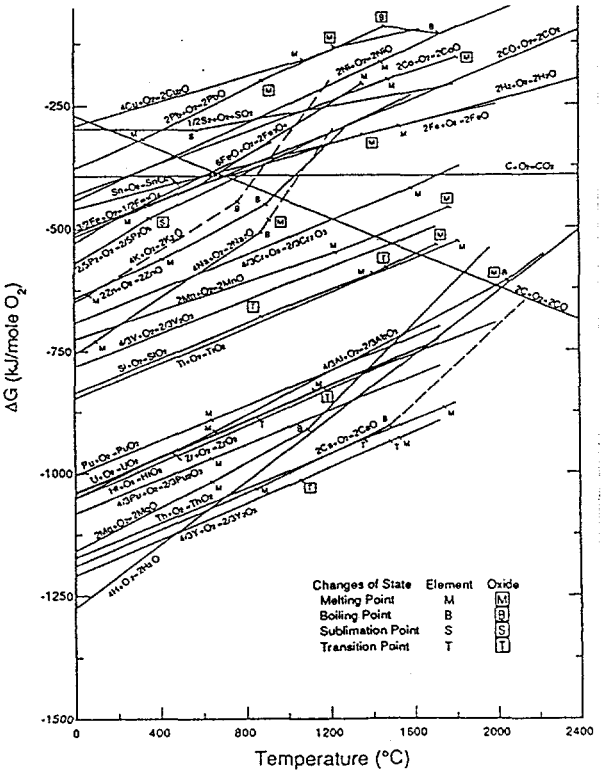


Figure 3: Ellingham-Richardson Diagram with Free Energy of Formation of Water using Monatomic Hydrogen

Experimental

Starting Material

The starting material for this investigation was obtained from Cabot Corporation. The material consisted of low grade high interstitial scrap powder. Mixed with the powder was other tantalum material with interstitial levels greater than the matrix composition. Figure 4 shows a cross section of the sintered logs. The light phase in the cross section is the very high interstitial material.

Figure 4: Macrograph of the starting material for this investigation. Note the light phase material which is very high interstitial content tantalum.

The blended composite mixture was pressed into billets then vacuum degassed. Attempts to electron beam melt the material were unsuccessful because outgassing significantly reduced beam intensity. The chemical composition of the starting tantalum is given in Table 1.

Table I Chemical Composition (ppm wt. %) of Tantalum Powder

Element	O	C	H
Composition(wt ppm)	10700	15810	6

Melting Parameters

Melt parameters were established based on viable commercial applications for the recycling of the tantalum powder. Melt rates were held to within an order of magnitude of conventional EB processing. Plasma gas selection was limited to compositions that could be easily handled in an industrial application. Power input; volts and amps, and torch profile parameters; standoff and articulation were held constant. A total of six plasma gas compositions were examined. Table 2 is a compilation of all melting and torch parameters.

Table II Melting and Torch Parameters Used in The Current Investigation

Melt Rates: 2.6 grams/s and 5.2 grams/s into a 100 mm dia ingot.
Gas Composition: He, He-3% H, He-6% H Ar, Ar-3% H, Ar-6% H
Power Input: Constant 150-165 V 540-510 amps
Torch Profile: Constant standoff Constant torch profile

Results

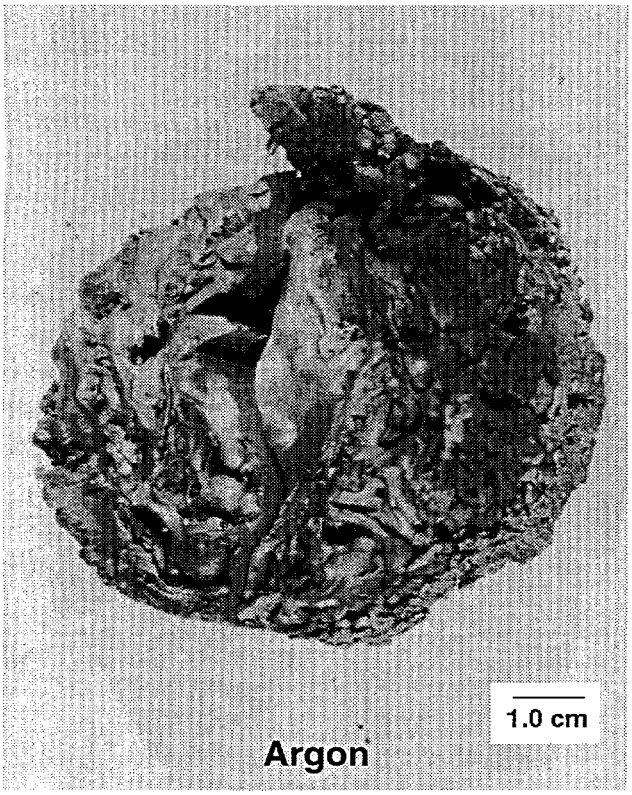
Melt Quality

Melt quality was determined based on observations of material splatter, depth of melt pool and melt pool geometry. Table 3 is a compilation of observations made during melting with various plasma gases. In general, melt quality with any of the helium gas compositions was superior to that of the argon gas even with hydrogen additions.

Table III Observations of Melt Quality During Melting of Tantalum Powder

Gas Composition	Observation
Ar	Poor melt quality. Only localized melting with considerable spatter.
Ar- 3H	Beginning of coherent melt pool. Material continues to spatter.
Ar- 6H	Well defined melt pool approx. 2 cm. depth. Minimal spatter.
He	Good plasma control. Good melt pool; 3 cm depth. No spatter.
He- 3H	Same as pure He but increased melt pool area and depth: 4 cm.
He- 6H	Excellent pool geometry. No spatter Pool depth apprx. 5 cm.

Qualitative differences in the melting can be seen in Figure 5 with a comparison of pure argon and helium plasma gases. Both ingots in the figure were melted at 2.6 grams/sec. The helium ingot shows a well established



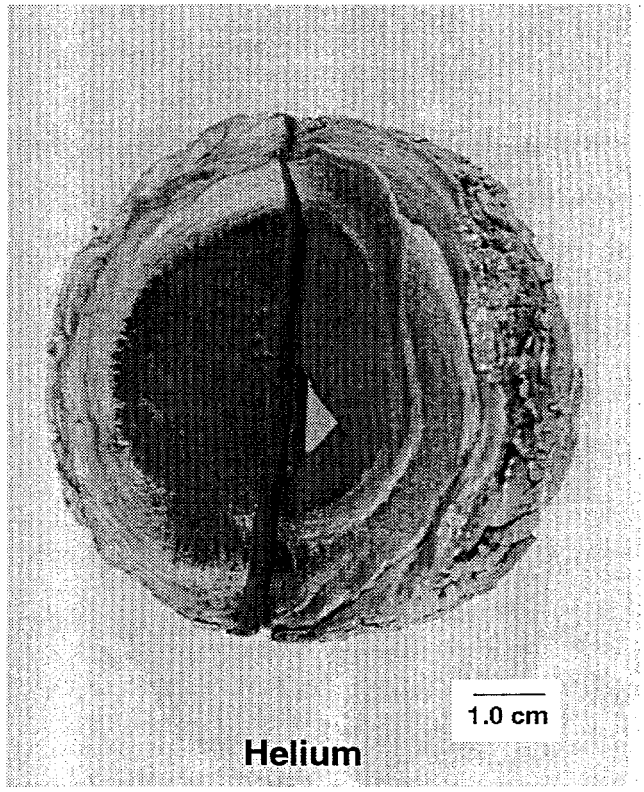


Figure 5: Macrograph of melted tantalum ingots using argon and helium plasma gasses. Melt rate was 2.6 grams/sec.

melt pool and smooth surface.The argon ingot never established a coherent melt pool and resulted in extensive spatter. The melt quality with the pure argon gas and fast melt rate, 5.2 grams/s, resulted in only a partially melted slug and extensive spatter during melting. Since the starting material could not be completely melted, no further analysis was performed on this material.

Ingot Chemistry-LECO Analysis

Each of the melted ingots were analyzed for final interstitial contents of carbon, oxygen, nitrogen and hydrogen. A concern before running the experiments was the possible pickup of hydrogen from the plasma gas therefore the analysis included this element. Each sample was removed from the center of the ingot by EDM and analyzed by LECO combustion techniques. Comparisons were then made for interstitial removal as a function of plasma gas composition and melt rate. In all cases nitrogen levels increased approximately 2000 ppm from the starting composition. Figure 6 is a plot of interstitial content for various plasma gases. All data is for the low melt rate of 2.6 grams/s. The interstitial content of the starting material is plotted for comparison.

Based on the starting chemistry for carbon and oxygen, complete reaction to form CO would result in a final tantalum oxygen composition of approximately 1600 ppm. The final interstitial compositions for all samples were above this level and not all of the carbon reacted. There are two possible explanations for the final chemistries. First, the melt rates were to fast to allow for the complete reaction. The work by Minura et.al (2) would support this hypothesis. In that work, melt rates were less than 1 gram/minute to achieve complete reaction. The second possibility is the inhomogeneity of the starting material. The higher interstitial content light phase seen in Figure 4, could easily skew the results depending on the phase distribution within the log.

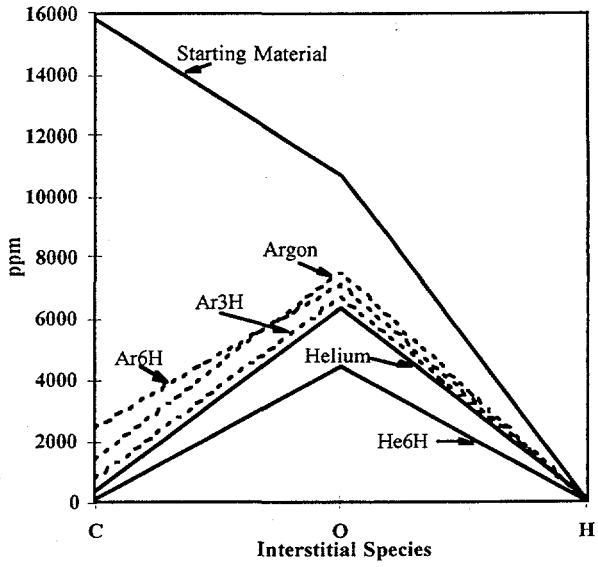


Figure 6: Interstitial content of the tantalum melted ingots as a function of plasma gas. All compositions are for the 2.6 gram/sec melt rate.

In spite of the variations in compositions, the plots in Figure 6 follow the general trend of lower interstitial content with increased hydrogen content in the cover gas. In addition, the helium gases are more effective in removing the interstitials compared to the argon series. These results are the same as the melt quality analysis and indicate that the higher heat content and thermal conductivity of the helium series gases are resulting in a hotter melt pool.

The hotter melt pool has three thermodynamic benefits for removing the carbon and oxygen. The higher melt pool temperature will thermodynamically enhance the formation of CO. An increase in temperature for this reaction results in an increase in the free energy of formation and will tend to drive the reaction further to completion. As the melt temperature increases, the tantalum oxide heat of formation will decrease making the oxide less stable. The reduction in free energy will allow further direct disassociation of the oxide compared to a lower temperature system. Finally, the monatomic hydrogen in the plasma gas will contribute to lowering the oxygen content by direct reduction. The hydrogen content in the final ingots remained low in spite of the relatively large amount of the gas introduced into the system. The compositions varied from 26 to 146 ppm hydrogen with no correlation to hydrogen content in the gas. Table IV shows the compilation of final interstitial chemistries for the 2.6 gram/s melt rate and six plasma gases.

Table IV Final Interstitial Content For The Low Melt Rate Tantalum Ingots

Plasma Gas	O	C	H
Ar	7541	1427	66
Ar-3H	6724	758	57
Ar-6H	7123	2466	23
He	6334	371	146
He-3H	6506	984	56
He-6H	4403	130	26

A comparison of the final chemistries with melt rate was made to determine a processing window which allows trade-offs of processing time and plasma cover gas. Figure 7 shows a plot of low and high melt rates for the three best plasma gases based on melt quality. In most cases, the lower melt rate resulted in lower interstitial content compared to higher melt rates.

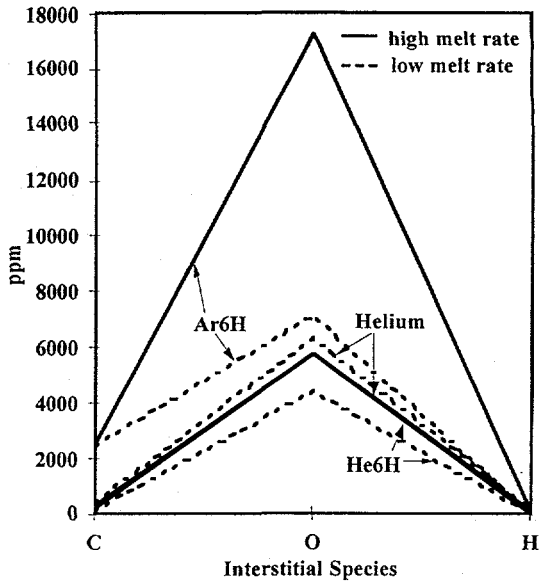


Figure 7: Variation in interstitial content for low and high melt rates and various plasma gases

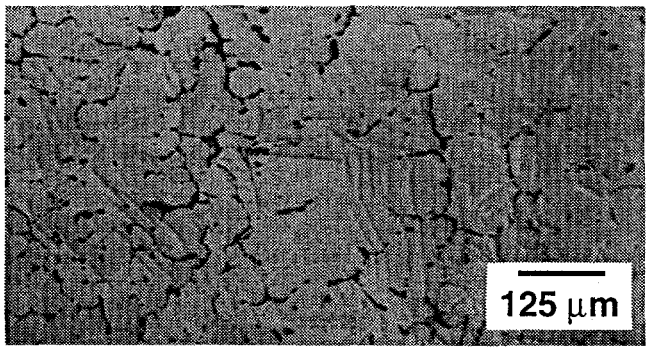
The maximum interstitial content for the next melting step will dictate the melt rates and plasma gases to ultimately be used for recycling.

Ingot Chemistry- Optical Analysis

Variations in chemical analysis results required a second method to qualitatively determine the interstitial content in the ingots. Since the melting point of all tantalum oxides is below that of tantalum metal, any large oxide slag inclusions would be trapped as a liquid at the grain boundaries. Therefore, an optical approach was taken to rank each ingot based on inclusion content, first in the unetched condition to show gross molten slag regions and then etched to reveal finer inclusions.

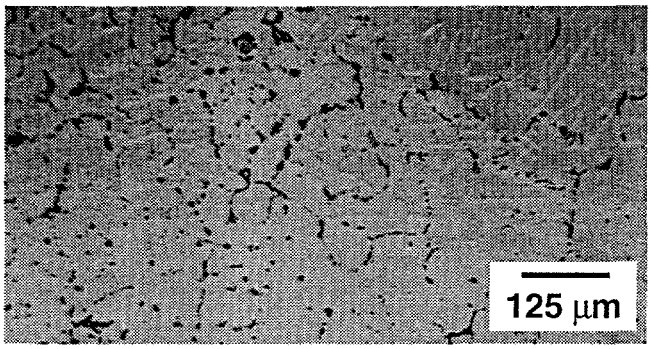
Figure 8 shows the unetched micrographs for the argon and argon-6 hydrogen plasma gases at the high and low melt rates. As was stated previously, the high melt rate using pure argon was not evaluated because of the poor quality and unmelted material in the ingot. The micrographs show the change in oxide content and morphology. This series confirms the trends in the chemical analysis with less oxide in low melt rate material as well as decrease in oxide content by the addition of hydrogen to the plasma gas. While the trends between both analysis are the same, the optical variations between ingots is much more pronounced than the LECO analysis results. For example, the total interstitial content difference between the pure argon and argon-6 hydrogen is approximately 500 ppm, however, the optical micrographs show a much greater variation than this amount. Figure 9 shows the same representation for the helium gas series.

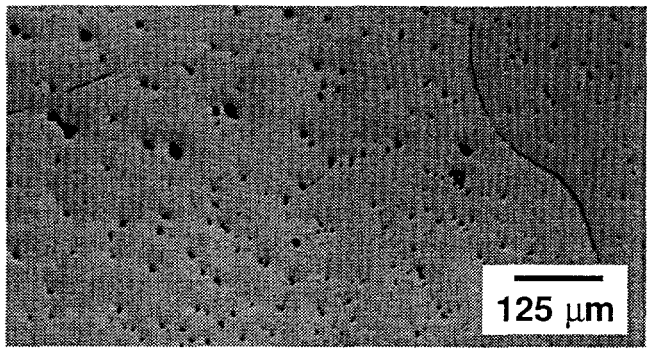
Not Determined



Ar long

Ar short

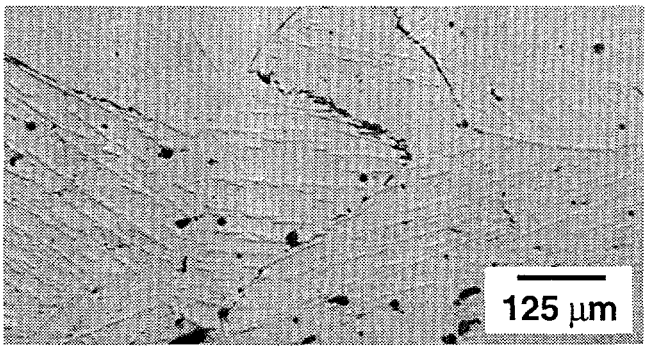




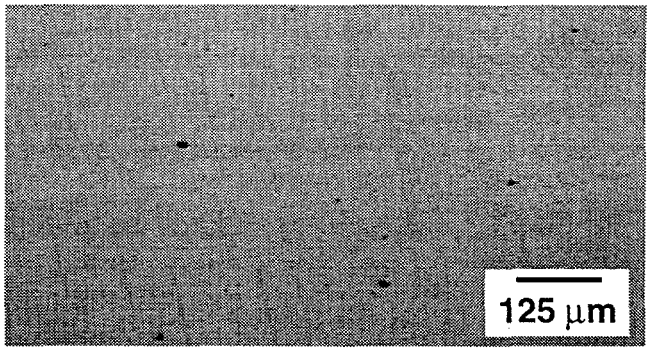
Ar-6H short

Ar-6H long

Figure 8: Unetched micrographs of tantalum ingots melted with various argon plasma gases.



He short



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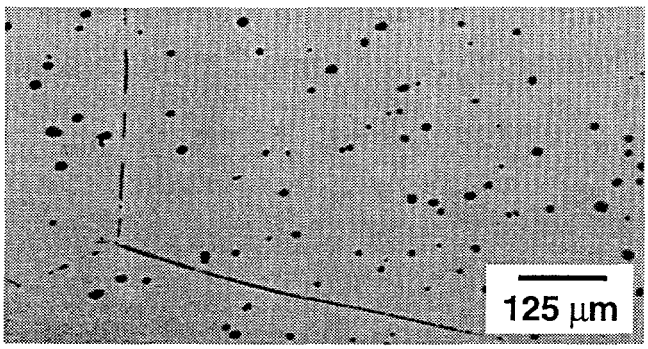
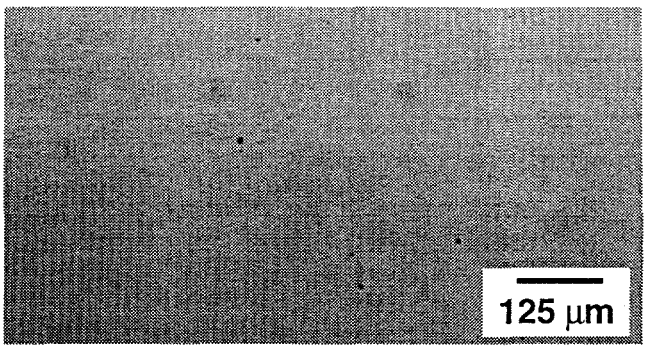


He-6H short



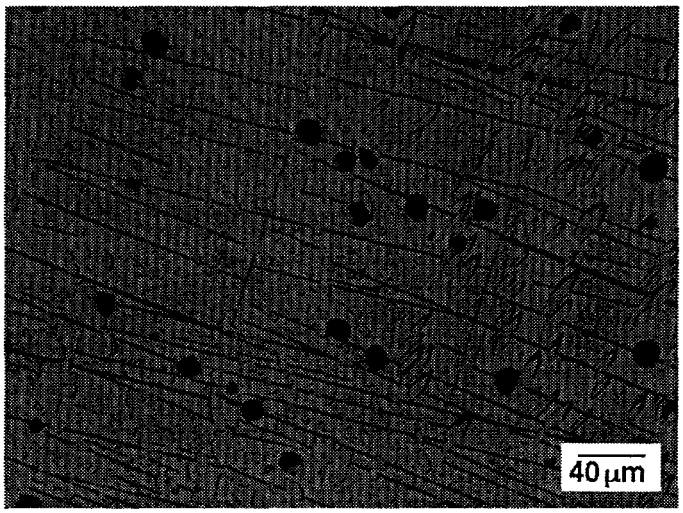
He-6H long

Figure 9: Unetched micrographs of tantalum ingots melted with various helium plasma gases

Inclusion/ X-Ray Analysis

Because of the large number and morphology variations in inclusions, two ingots were selected for X-ray diffraction characterization. Figure 10 shows a representative microstructure of the tantalum ingot melted with pure argon gas and the low melt rate. Under the micrograph is the X-ray diffraction pattern for this sample. The diffraction pattern confirmed the presence of all three tantalum oxides, TaO, TaO_2 and Ta_2O_5 in varying amounts with TaO the most abundant. The presence of TaO is suprising since this oxide is not thermodynamically stable at room temperature based on the literature (10). In addition, lines for tantalum carbide and tantalum nitride are also present. At least three different second phase morphologies are present in the micrograph. Based on the diffraction patterns, the elliptical light phase is TaO and the dark spherodized inclusions are Ta_2O_5. The light phase lining the grain boundaries is possibly TaO_2.

The second sample analyzed was from the ingot melted with He-6H again at the low melt rate. Figure 11 shows the representative microstructue for this sample and the corresponding diffraction pattern. The microstructure is much cleaner with no visible second phase. The diffraction pattern for this sample shows only tantalum, tantalum nitride and possibly a very low tantalum oxide,Ta_6O. Since many of the lines for tantalum metal and tantalum compounds overlap, the presence of the low oxide is based on one line, however, the line is only representative of Ta_6O.



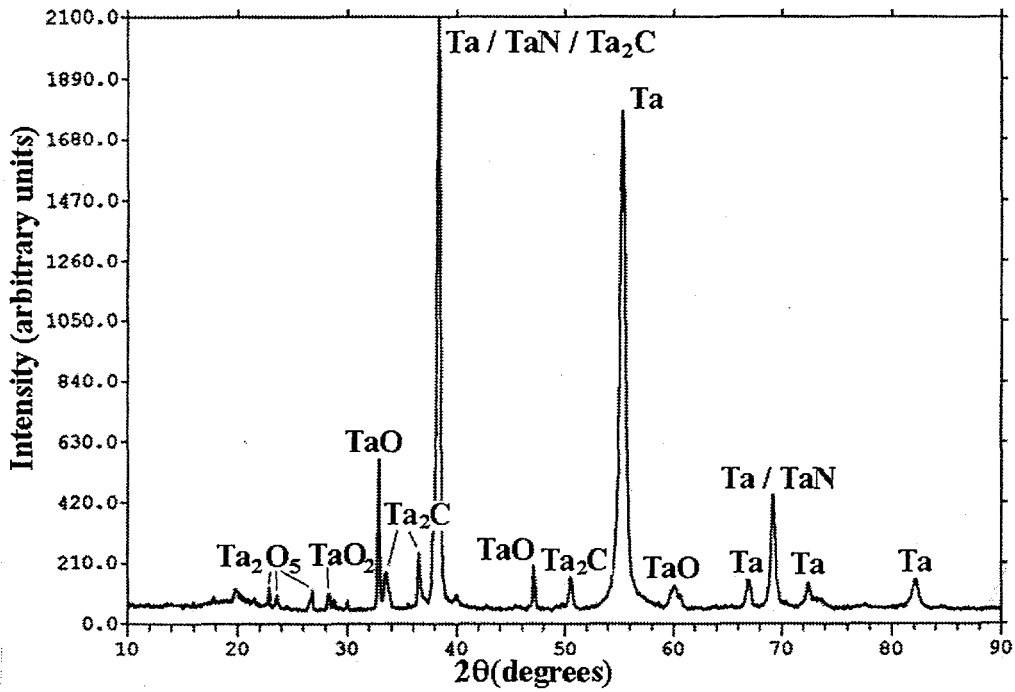
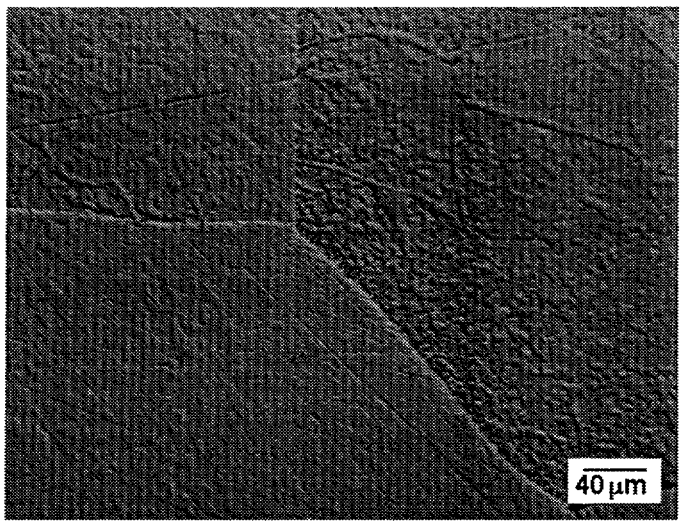


Figure 10: Micrograph and X-Ray diffraction lines for tantalum ingot melted under Argon/low melt rate.



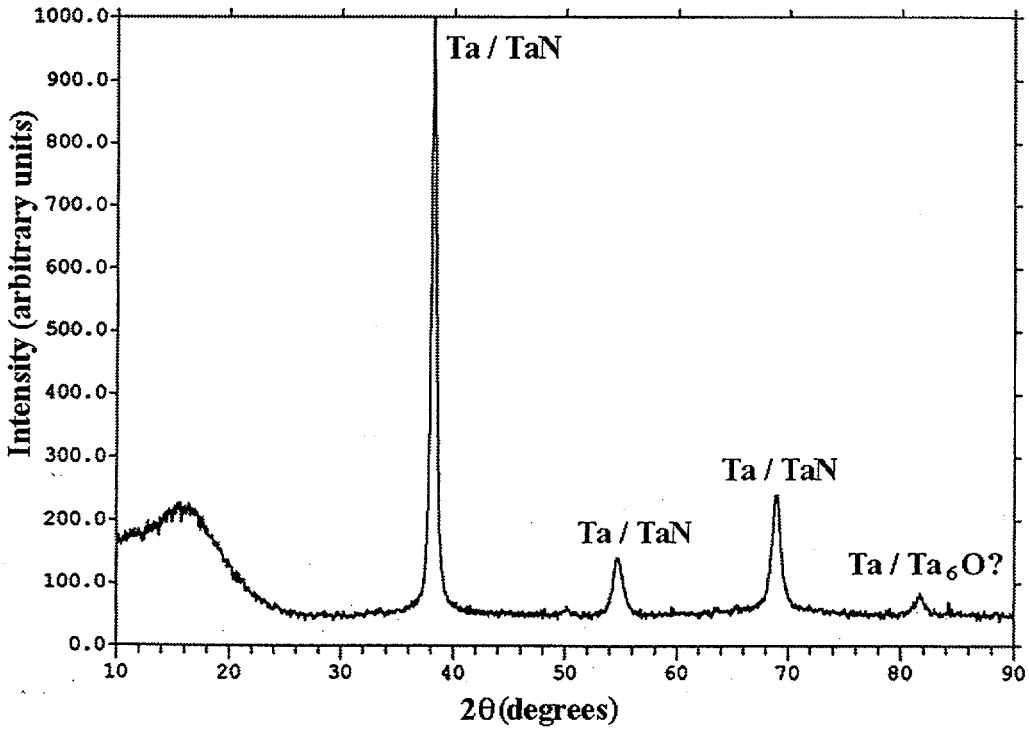


Figure 11: Micrograph and X-Ray diffraction lines for tantalum ingot melted under He-6 H/low melt rate.

Summary

The current work indicates that plasma arc melting offers a viable processing approach for the recycling of high interstitial/contaminated tantalum powder. While the interstitial levels in the melted ingots were still high, the plasma melting lowered the oxygen and carbon to a level acceptable for subsequent electron beam melting. Based on the parameters in this study:

a) Plasma arc melting is the only alternative for melting high interstitial content material due to excessive outgassing.

b) Pure argon is the least efficient plasma gas based on melt quality or interstitial removal. Compositions of argon-hydrogen gases are acceptable based on melt quality but at lower melt rates than considered in this work.

c) He-6 H plasma gas produced the best melting results and the greatest reduction in interstitial content at the 2.6 gram/s melt rate.

d) Hydrogen uptake in the tantalum ingot, due to additions in the plasma gas, is minimal.

Acknowledgments

The authors wish to acknowledge Ann Kelly for the excellent metallographic preparation and Julie Bremser for the X-Ray diffraction analysis. The authors aknowledge Chris Michaluk of Cabot Corporation for supply the feed material, interstitial analysis and helpful discussions on the thermodynamics of tantalum oxide. This work was conducted under the auspices of the U.S. Department of Energy.

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