Refractory Metals Fabrication Technology as Applied to Fusion Reactors

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Pacific Northwest Laboratories

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**REFRACTORY METALS FABRICATION
TECHNOLOGY AS APPLIED TO
FUSION REACTORS
A STATE-OF-THE-ART ASSESSMENT
FINAL REPORT**

15 MAY 1975

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SUBMITTED IN COMPLIANCE WITH CONTRACT NUMBER BSA-921

PREPARED FOR:
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FOREWORD

This Final Report was prepared by McDonnell Douglas Astronautics Company - East (MDAC-E) under the Battelle, Pacific Northwest Laboratories Contract BSA-921, State of the Art Assessment of Refractory Metal CTR Component Fabrication Processes. The Study Leader at MDAC-E was Mr. John Davis and final report author was G. W. Wille. The program was a six-month effort during the period 15 October 1974 through 15 May 1975.

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SUMMARY, ASSESSMENT AND RECOMMENDATIONS

SUMMARY

Developments leading to a thermonuclear reactor for energy production have been underway for the last 15 to 20 years. Much of this activity was carried forward by the scientific community and was related to the investigation of concepts for containing and heating a plasma to achieve hydrogen fusion under controlled conditions. The recent emphasis on energy, caused by the realization that fossil fuels will be in short supply and the national goal of self sufficiency in this century has spurred the Energy Research and Development Administration (ERDA) into engineering studies of fusion energy producing devices.

The work described in this report focused on the material fabrication requirements for the first wall/blanket structure of a controlled thermonuclear reactor (CTR). This work concentrated on the commercially available refractory metal alloys of molybdenum, niobium, tantalum and vanadium. It has been postulated that these materials have potential for withstanding the aggressive environment in a CTR, consisting of a high temperature, very high energy neutrons, chemically aggressive coolant, high vacuum and thermal cycling. The ability of the refractory metals to operate in excess of 1000°C should, by itself, provide improved operating efficiencies for a CTR, compared to stainless steel, and hastens their early consideration for the first wall/blanket structural material.

Much of the development and fabrication of the refractory metal alloys was accomplished by the aerospace industry starting in the mid-to-late 1950's. Accordingly, this report is a compendium of information gathered from aerospace and other industry and government activities as it relates to the fabrication practices for the four refractory metals previously noted.

ASSESSMENT

A general assessment of the refractory metal fabrication technology as it exists today yielded few surprises, and are summarized in the following paragraphs.

The basic fabrication processes for molybdenum, niobium, tantalum and their alloys have been investigated and established on a limited scale. None of these processes have been used on large components or for large scale production. Compared with steel or aluminum fabrication procedures, the fabrication of refractory metal structures would be in the development stages. Most of the processes for molybdenum and niobium have been developed for reasonably small aerospace components and reactor test apparatus under very closely controlled shop and laboratory conditions. These procedures are well documented and will provide a good starting point for the development of fabrication procedures for specific CTR components. They also provide a good basis for assessing the fabricability of these two alloys. Tantalum has been used primarily in the chemical process industry for fabricating or lining tanks, valves, or piping. The use of tantalum for airframe components is limited because of its poor structural efficiency until temperatures exceed 1500 to 1600°C. Vanadium was developed specifically for nuclear applications, and very little specific information was found on fabrication practices.

Findings that apply to the refractory metals, in general, as they might be used in CTR first wall/blanket structures are:

- 1) Most of the development and structural fabrication activities were concerned with very thin-gage materials, ranging in thickness from near foil .025 mm (.010 inch) to a maximum of 1.5 mm (.060 inch) for sheet metal. Many of the proposed CTR first wall/blanket designs call for thicknesses in excess of 2.5 mm (.100 inch). These changes in thickness cause perturbations in the allowable fabrication limits just as they do in the more conventional materials. Additionally, the difference in gage will also affect the primary rolling parameters for the alloys of interest, especially in molybdenum, and might cause additional metallurgical changes deleterious to fabrication characteristics.

2) A significant problem might arise because of the small sheet sizes available in the refractory metals. For instance, the normal maximum sheet widths available for molybdenum are 55.9 cm (22 inches) while for niobium and tantalum it is about 76.2 cm (30 inches). This presented no significant problem to the aerospace industry, at the time, because the vehicles fabricated were relatively small and/or of limited quantity. Conversely, the first wall/blanket of a CTR can be extremely large and might not be efficiently fabricated from the small sheet sizes available. This would depend upon the specific first wall/blanket design. In any event, a scale-up of sheet sizes could require a major effort by the primary alloy producers.

3) The refractory metals are sensitive to small amounts of interstitial contamination by carbon, oxygen, hydrogen, or nitrogen. Contamination results in a brittle behavior of the metals. To prevent contamination during elevated temperature processing, extreme care is necessary in the form of cleanliness prior to the temperature exposure and a controlled atmosphere during elevated temperature exposure. Equipment and facilities are presently available that meet the cleanliness and atmosphere requirements, however the limiting factor for CTR use will be part size. The sizes of the working zone in currently operating vacuum furnaces suitable for refractory metal fabrication are up to 2.1m dia x 2.4m high (84 in dia x 96 in high) for up to 1538°C (2800°F) and 1.3m dia x 3.04 m high (52 in dia x 120 in high) for up to 1649°C (3000°F).*

Each of the alloy systems investigated have their own characteristics which require some additional detailed assessment of the existing state-of-the-art.

Molybdenum and its alloys can be produced by either powder metallurgy or arc-cast techniques. Currently, the majority of molybdenum is produced by arc-cast techniques because the material properties are generally superior.

*Telephone conversation with Mr. R. Marsh, Wah Chang Albany, Albany, Oregon.

Molybdenum and its principal alloy Molybdenum-TZM are the strongest and most difficult to form of the refractory metals of interest. In addition, the ductile-to-brittle transition temperature (DBTT) is strongly affected by prior work history. Since the rolling process is used to control both the strength and ductility of the material as well as the DBTT, it is probable that additional work is required to develop the rolling parameters to successfully and reproducibly fabricate parts of consistent quality in the range of thicknesses required for CTR's.

The blanking of molybdenum sheet stock must be carefully controlled to prevent delaminations from initiating at a cut edge which may propagate during subsequent forming or use. It has been found that bandsawing, electrical discharge machining, electromechanical machining and chemical milling are preferred blanking methods compared to punching or shearing.

To prevent cracking, the forming of molybdenum sheet is usually performed at moderately elevated temperature (93 to 395°C) depending upon the prior work history, gage and forming process. The edges and surfaces must be free of defects which act as stress concentration points which may lead to part failure during forming.

A severe limitation on the use of molybdenum centers on the problems associated with metallurgical joining. The coolant and vacuum-tight requirements of the CTR first wall/blanket system indicate the use of metallurgical rather than mechanical joints. Fusion welding is at best a tenuous process, since the recrystallized and large grain structures in the weld and heat-affected-zone result in a DBTT well above room temperature. Arc-cast material is preferred to powder metallurgy material for welding because of the lower impurity level and therefore less resultant weld porosity. Brazing may alleviate the recrystallization problem, if braze alloys are used that flow below the recrystallization temperature. However, braze techniques may be difficult to develop and implement on large structure, especially for field assembly and repair operations. In addition, the characteristics of the braze alloy in the CTR nuclear

environment must be carefully assessed to ensure that unwanted radioactive species are eliminated, and that deleterious defect formation (swelling, embrittlement, gas formation) is not inherent in the braze alloy chemical composition.

Niobium, tantalum and vanadium and their moderate strength alloys of interest are all ductile, relatively easy to fabricate materials. Their forming and machining characteristics are somewhat similar to stainless steel. They all have a high solubility for carbon, oxygen, nitrogen, and hydrogen at elevated temperature, and a low tolerance for these interstitial elements at room temperature. Accordingly, all high temperature operations such as heat treating, welding, brazing, or diffusion bonding should be done in a controlled atmosphere of either purified inert gas or vacuum of 1.33×10^{-4} Pa (10^{-6} torr). If high temperature operations are performed in air, a sufficient amount of surface metal must be removed to eliminate the embrittled layer at the surface. Some niobium alloys are more tolerant of interstitials than others; this point should be considered when selecting an alloy.

Of these three ductile refractory metals, there is very little, if any, published data available on vanadium forming limits, machining techniques, or joining methods.

RECOMMENDATIONS

The state of the art assessment of the fabrication methods, for the four refractory metal systems studied, has yielded some specific recommendations for additional research and development activities. For all four of the refractory metals and their alloys, problems arise that should be addressed in a timely fashion.

1) Virtually no data is available that describes the effect of forming on the subsequent radiation damage properties of finished parts. For instance, it has been established that cold worked stainless steel is less prone to swelling and embrittlement in a high neutron flux environment than it is in the annealed condition. It has been shown that the tritium bulk diffusion rate in stainless steel is markedly increased by cold work, which might possibly lead to problems of tritium containment. Furthermore, it is known that cold work with the associated residual stresses can adversely affect compressive yield strength (Bauschinger effect), fatigue life, corrosion, stress corrosion cracking susceptibility, metallurgical stability, ductility and creep resistance. None of the literature surveyed addressed these considerations. Until post fabrication properties are related to the nucleonic, metallurgical, and mechanical behavior, the best fabrication procedures for long life refractory metal systems cannot be established.

2) Forming practices should be established for the refractory metals in the thicknesses of interest. This would include key material properties determinations such as work hardening rate, uniform elongation, short gage length elongation and total strain to-failure. Basic forming methods such as bending, dimpling, stretch forming, drawing and beading should be accomplished on sufficiently large pieces to verify fabrication predictions derived from the simpler materials tests.

3) Field assembly and repair methods for the CTR first wall/blanket is required because of size and the need for periodic replacement. Metallurgical joining of the first wall/blanket components will be accomplished

in a closely controlled environment. Ultimately, the first wall and blanket structure will have to be erected and assembled in the field. Field welding or brazing techniques for assembly or repair have not been addressed for the refractory metals of interest. This activity must be pursued until techniques are developed to make field assembly methods as straightforward as they are for stainless steel.

4) Welding the heavier gages associated with CTR first wall/blanket systems will require the development of multipass procedures. This is an important area since improper multipass welding methods will probably increase the DBTT of all these materials, which will likely affect the suitability of materials for CTR use.

Molybdenum, specifically, requires a major emphasis in metallurgical joining. Programs attacking three major areas of joining technology are required.

In fusion welding, work should be done to minimize or eliminate the unwelcome change in DBTT caused by recrystallization. This would infer work in the area of special weld filler metal chemistry (including inoculants), high frequency pulsed arc welding procedures, and the development of inexpensive alloys that have a higher tolerance to recrystallization embrittlement.

Solid state methods of assembly should be developed to eliminate the recrystallization problem. This should include experimental work in inertia welding (where geometry permits), solid state diffusion bonding, explosive welding, liquid interface diffusion bonding, forged upset diffusion joining, and roll diffusion bonding. Many of these techniques have been developed for more conventional metal alloys and should be adaptable to molybdenum (and the other refractory metals, if needed).

Brazing should be further investigated to develop braze alloys that will provide the necessary strength at operating temperatures without requiring braze temperatures in the recrystallization range of molybdenum.

In addition, and perhaps more importantly, the braze alloys should be of a chemical composition that will not contain elements that have long lived radioactive species that result from neutron activation. Radiation damage characteristics must also be considered. Brazing methods should also be developed that are adaptable to field assembly and repair methods.

INTRODUCTION

The current interest in controlled-thermonuclear-reactors (CTR's) has generated a need for materials suitable for fabrication into the first wall/blanket structure of the reactor.

The first wall/blanket of a CTR is essentially an energy converter which is coupled to the plasma or energy producer. The first wall usually provides a vacuum tight enclosure for the plasma. Contained in the 1st wall and blanket region are materials for breeding tritium and moderating neutrons and coolant channels to remove the heat. The structural material used in the first wall and blanket region must be compatible with the reactor coolant and breeder materials at elevated temperatures. The material must have reasonable thermal conductivity to avoid high temperature gradients and it must maintain structural integrity despite radiation damage, corrosion and elevated temperature exposure.

The refractory metals are considered prime candidates for use in controlled thermonuclear reactors (CTR) because of their strength at high temperatures and compatibility with liquid metal coolants. The candidate refractory metals are molybdenum, niobium, tantalum, and vanadium and their alloys. Before specific refractory metal alloys can be selected and designs incorporating refractory metals can be effectively accomplished, an assessment is necessary to determine the capability for fabricating these metals into the types of configurations that would be used in a CTR first wall/blanket structure.

A basic understanding of the refractory metal characteristics will enable the user to better understand why certain procedures are necessary to produce acceptable structures. The refractory metals have a body-centered cubic (bcc) crystal structure which is characterized by a transition from ductile to brittle behavior over a relatively narrow temperature range. The ductile-to-brittle transition temperature (DBTT) is not a simple invariant property of a given alloy composition; it is a function of the composition, impurity level, microstructure, entire

thermomechanical fabrication history of the material, operating conditions and part configuration (stress concentrations) and the limit of ductility which is used to indicate brittle behavior. It is the DBTT and its ramifications that must be primarily considered when fabricating the refractory metals.

Molybdenum and its alloys in a fully annealed and recrystallized condition have a transition temperature above room temperature. Cold working will lower the transition temperature to below room temperature. As a result, molybdenum and its alloys are generally used in a cold worked and stress relieved condition. Welding will recrystallize molybdenum causing a DBTT above room temperature. Niobium, tantalum, vanadium and their alloys of interest in this study have a DBTT well below room temperature when in an annealed condition, however, the DBTT is raised considerably by interstitial contamination from carbon, oxygen, hydrogen, and nitrogen. Therefore, elevated temperature processing such as welding must be carefully controlled to prevent embrittlement.

The refractory metals were the recipients of much research and development during the period of 1955 through 1968. One such program was the Department of Defense Refractory Metals Sheet Rolling Program. The development of sheet metal fabrication practices progressed simultaneously with primary fabrication and alloy development by suppliers in an attempt to develop more fabricable alloys. As manufacturing processes and quality of sheet improved, the response of the sheets to fabrication changed. With improved uniformity from sheet-to-sheet, fabrication processes were developed to produce acceptable parts without excessive scrap rates. Much of the R&D work was government sponsored and primarily oriented to aerospace products and requirements. Some of the work was for classified projects and therefore the information is not readily obtainable for release. The downgrading of classified information until it is unclassified generally takes 12 years. Since much of this work was conducted in the early 1960's, portions of the investigations could be expected to be released in the near future.

The purpose of this study is to assess the current state-of-the-art of secondary fabrication techniques useful for fabricating the CTR's. This

study considers those fabrication techniques necessary to fabricate mill products such as sheet, rod, bar, tubings and forgings into a final product.

The fabrication methods investigated are:

- Inspection
- Blanking
- Edge Preparation
- Forming
- Machining
- Joining
- Cleaning
- Heat Treating or Thermal Processing
- Coating

This report is a review of the available information from reports and articles extracted from extensive literature searches, from direct contacts with industry suppliers, and from users of the refractory metals. The sources and contacts made are listed in Table 1. The major emphasis has been placed on the more recent publications because of the improved fabrication techniques and alloys that evolved as the refractory metals were used.

This program was sponsored by Battelle-Pacific Northwest Laboratories. A companion investigation of primary fabrication processes was performed by Battelle-Columbus.

The following parts describe the findings of this study.

Tables listing the alloy designations and compositions for niobium and tantalum alloys are presented in Appendix D to familiarize the reader, since many of the early alloys are no longer commercially available.

The conversion factors used for the International System of Units are presented in Appendix E.

TABLE 1. INFORMATION SOURCES

<u>LITERATURE REFERENCES</u>	<u>DIRECT CONTACTS</u>
° Atomic Energy Commission Abstracts*	Air Force Materials Laboratory
° Defense Documentation Center*	Argonne National Laboratory
° Government Industry Data Exchange Program	Boeing Aircraft Company
° Machinability Data Center*	American Metals Climax Inc.
° McDonnell Douglas Corp. Library*	Fansteel Inc., Metals Division
° Metals and Ceramics Information Center*	Foote Mineral Company
° National Aeronautics and Space Administration*	Lawrence Radiation Laboratory
° Report and Article References	Los Alamos Scientific Laboratory
	Machinability Data Center
	Materials Advisory Board
	McDonnell Douglas Corp.
	Nardon Manufacturing Company
* Extensive Bibliographies	Naval Air Systems Command
	Naval Bureau of Weapons
	Nooter Corp.
	Oak Ridge National Laboratory
	Precision Sheet Metal, Div. of Fansteel
	Refractory Metals Welding Company
	GTE Sylvania
	Teledyne Wah Chang Albany
	Teledyne Wah Chang Huntsville
	Union Carbide

PART I - MOLYBDENUM

MOLYBDENUM OVERVIEW

Unalloyed molybdenum and Mo-TZM alloy (Mo-0.5Ti-0.08Zr.030) are the only commercially produced forms of molybdenum at the present time. Molybdenum and Mo-TZM possess a promising combination of properties to meet the requirements of the CTR first wall/blanket structure. Additionally molybdenum has a singular advantage of being the only refractory metal in plentiful supply within the continental United States.

Molybdenum and its alloys can be produced either by powder metallurgy or arc-cast techniques. Currently, the majority of molybdenum is produced by arc-cast techniques because the material properties are generally superior. During the mid-1960's considerable effort was expended (sponsored by Bureau of Naval Weapons) to develop and improve the fabrication characteristics of the refractory metals particularly the molybdenum alloys. As a result of this effort, the formability of molybdenum, its alloys, and especially TZM were greatly improved. Because of the vast difference in fabricability of molybdenum and TZM before and after the extensive effort, one must be aware that data on fabrication presented on so called "old" material will indicate inferior fabricability, especially formability, to that presented on "new" material supplied after the government-funded effort. Data generated after 1965 could generally be considered "new" material with improved fabricability. One can make a reasonable assumption that the material produced more recently will have even better fabricability because of improved processing techniques. Because the formability was greatly affected by the time at which the material was produced, an attempt has been made to indicate if the material referenced in the forming section of this part of the report represents old technology or new technology as an aid to assessing the referenced forming characteristics.

The single greatest deterrent to the use of molybdenum is its ductile-to-brittle-transition behavior at or above room temperature when in the fully annealed and recrystallized state. The ductile-to-brittle

transition temperature (DBTT) is affected by metallurgical variables such as composition, impurity content, grain size and morphology as well as other properties related to the total thermomechanical history of the material. The DBTT is also strongly affected by stress state and strain rate. The major difficulties in fabricating molybdenum have been associated with brittle behavior from too high a DBTT, which in turn might have been aggravated by improper strain rates during forming, a high degree of biaxial or triaxial stress state caused by bending, holes or notches, or a non-optimum grain size. Normally, molybdenum and Mo-TZM are used in the cold worked (80-90% reduction) and stress relieved temper. This thermomechanical working lowers the DBTT to below room temperature (Figure I-1). Unidirectional cold working causes planar anisotropy (Figure I-2).⁽¹⁾ Cold working also induces high internal stresses that result in a high propensity for delamination, especially at the edges.

The nearness of the DBTT to room temperature usually dictates that many forming operations be performed between 93 to 260°C (200 to 500°F), depending on the severity of the forming.

Because of the internal stresses in the cold worked and stress relieved material, there is a propensity to delaminate during some blanking operations such as shearing. This necessitates care during the blanking operations. Blanking can be accomplished by bandsawing, provided sufficient backup is provided to the material in order to minimize vibration.

Fusion or resistance welding and some brazing operations cause complete recrystallization and grain growth which raise the DBTT to well above room temperature. Because the 1st wall/blanket structure must be vacuum tight, the designs require considerable welding or brazing, thus this characteristic must be carefully considered.

In spite of these seeming difficulties, molybdenum and molybdenum alloys have been fabricated into complex structure in the aerospace industry. For example, workers at McDonnell Douglas Astronautics Company

FIGURE I 1. EFFECT OF ROLLING REDUCTION ON THE BEND-TRANSITION TEMPERATURE OF TZM SHEET

FIGURE I 2. BEND-TRANSITION BEHAVIOR OF STRESS-RELIEVED AND RECRYSTALLIZED TZM SHEET

MOLYBDENUM STRUCTURAL CYLINDERS AND BOX

ALL DIMENSIONS IN CM

SKIN — 0.025 Mo — 0.5% Zr
CORRUGATION — 0.025
END RINGS — 0.18 FS 82 Nb-32 Ta-1 Zr

ALL MATERIAL
SKIN — 0.025 Mo — 0.5% Zr
CORRUGATION — 0.025
SPAR & RIBS — 0.10

FIGURE I-3 MOLYBDENUM STRUCTURAL CYLINDERS AND BOX

FIGURE I-4 MOLYBDENUM (TZM) CONTROL SURFACE

have fabricated complex molybdenum TZM parts for flight vehicles. See Figures I-3 and I-4.

The following sections discuss the fabrication processes developed for molybdenum and Mo-TZM alloy. Where helpful, past difficulties and their solutions are presented. In some cases, data for Mo-0.5Ti is presented, since much work was done on this alloy for the X-20 (Dyna Soar hypersonic glider)⁽³⁾ program prior to the development of Mo-TZM.

1.0 INSPECTION

Inspection is necessary to verify that the incoming material has the proper strengths and, especially important for the refractory metals, that the materials have certain characteristics that enhance the ease of future fabrication processes.

The most important characteristic for molybdenum and its alloys is the DBTT. When the DBTT is sufficiently low (near or below room temperature) adequate formability at elevated temperatures can be expected. Bend tests are generally used to determine DBTT.

The proper choice of inspection methods is important to help assure the quality of the materials or structure. It will be necessary to decide what quality requirements must be met for both incoming material and fabricated structures.

To assure the desired quality for incoming material, it is necessary to have a mutual understanding between the consumer and the producer of what is required and what is producible. The specification should state clearly the tests and results that are required for acceptable material. A McDonnell Material Specification, MMS 184, for TZM strip, sheet and plate is included (Appendix A) as an example specification.

MDAC-E⁽²⁾ have found that modified inspection procedures had to be implemented for refractory metals. For example, they found that inspection for delaminations were much more effective when visual inspections were conducted using a stereo binocular with magnification up to 30X. Training programs were established to instruct personnel in handling and storing these materials. Coated and uncoated molybdenum hardware was handled with white nylon gloves and sealed in a polyethylene bag to avoid contamination and more importantly, to distinguish this material from the more common metals normally handled by the workman.

Considerable effort was also expended during the X-20 (Dyna-Soar)

program⁽³⁾ at Boeing Aircraft in developing procurement specifications for refractory alloys that would ensure the receipt of high-quality material and yet be within the capability of the suppliers.

The inspection techniques discussed may apply to incoming material specifications or for in-process inspections during fabrication. The inspection tests may be classified broadly into three categories as follows: 1) non-destructive, 2) chemical, and 3) mechanical or destructive. Typical non-destructive tests include visual, dimensional, flatness, waviness, surface roughness, penetrant, radiographic, eddy current, ultrasonic and helium leak check. Typical mechanical and destructive tests include metallography, hardness, tensile, creep and bending.

1.1 Non-Destructive Tests

Dimensional, flatness, waviness and surface roughness tests are conducted primarily on incoming material. The flatness and waviness are important for sheet and plate. If excessive, these factors could create difficulty during forming operations. Surface roughness or finish is also important for best formability. Normal flatness requirements for TZM are 4 percent maximum. That is, the vertical distance between a high and a low spot was not allowed to exceed 4 percent of the horizontal distance between them. Thickness tolerances generally reflected sheet width. An example of typical tolerances are shown below (MMS 184 Appendix A):

Thickness Tolerances, mm (Inches) Plus or Minus			
Nominal Thickness		Width Ranges, cm (inches)	
(mm)	(Inches)	35.6 & Under (14 & Under)	30.5-61.0 (12-24)
.28 and under	0.011 and under	--	*
.30-.49	0.012 to 0.019	.038 (.0015)	*
.50-.75	0.020 to 0.029	.050 (.002)	*
.76-.99	0.030 to 0.039	.060 (.0025)	*
1.00-1.26	0.040 to 0.049	.076 (.003)	*
1.27-2.53	0.050 to 0.099	7.5%	*
over 2.54	Over 0.100	10%	*

*AMS 2242, Table II

Other non-destructive tests such as dye penetrant, radiography, eddy current, and ultrasonic are relatively standard, and are adequately covered by existing government and industry specifications.

1.2 Chemical Analysis

Chemical analysis on refractory alloys, especially for the interstitial elements, has been a problem. The selection of samples for analysis and the methods used for analysis yielded variations in results from laboratory to laboratory. The variations were especially significant at low interstitial levels. Because small amounts of interstitial elements can have a marked effect on the fabricability of the refractory metal, accurate analysis is very important. Newer analytical techniques and equipment discussed later have lessened this problem.

Another potential problem associated with the analysis of interstitials is surface contamination that may occur during working and fabricating. It is possible that a thin surface layer may be highly contaminated, and yet not be detected during a bulk analytical analysis because even though the interstitial may have a high concentration on the surface, it represents only a small percentage of the total bulk sample. A highly contaminated layer can seriously effect subsequent forming and joining operations as will be discussed later.

It was found that surface contamination (interstitial) present on commercially produced sheet effects the formability of TZM and that its removal improved bend ductility. Surface grinding, originally specified for contamination removal, was discontinued in favor of pickling when it was demonstrated in flanging tests that pickled sheets were superior to ground sheets. Other difficulties with ground sheets were: (1) non-uniform metal removal and, hence, gage, flatness, and residual contaminated-area problems; (2) notch effects; and (3) problems at the producers mill which result in delayed delivery. The specified method of detecting surface contamination consisted of recrystallizing specimens sufficiently to produce 70 to 90 percent recrystallization in the core. The existence of regions of retarded recrystallization at or

near the surface was considered evidence of contamination. No surface contamination was permitted, sampling being done on a lot basis. Examination of 45 of the 253 sheets of Mo-0.5% Ti showed that 29 of them were contaminated in varying depths up to 0.1 mm (0.004 inch).⁽³⁾

Several methods are available to determine surface conditions, however, they require operations other than strictly chemical analysis.

These methods include:

- Metallography.
- Machining away all but the surface layer which is then analyzed.
- Auger spectrographic analysis of the surface.
- An indirect method of processing very thin samples with production parts and then analyzing the test sample in bulk.

The methods that are useful for determining the interstitial element contents are as follows:^(5, 6)

Hydrogen - vacuum extraction

Oxygen - inert gas or vacuum fusion

Nitrogen - Micro-Kjeldahl

Carbon - Combustion of refractory metal by resistance or induction heating in a stream of oxygen and then measure the CO₂ produced by conductimetric, coulometric or infra-red absorption techniques.

Because of the poor consistency and poor repeatability of interstitial analysis obtained from different laboratories, the Materials Advisory Board in support of the Refractory Metals Sheet Rolling Program⁽⁷⁾ and the Advisory Group for Aerospace Research and Development of NATO⁽⁸⁾ conducted surveys on methods of analysis for refractory alloys. These publications should be consulted for details.

1.3 Mechanical Testing

In general, the mechanical properties tests are the conventional procedures of tensile, bend, hardness, and creep at elevated temperature and metallographic examination. The National Materials Advisory Board Report MAB-192M makes recommendations toward standardization of test procedures for refractory alloy sheet materials.

1.3.1 Tensile Tests - When reporting the results of tensile tests, it is important that the strain rate be included because the ductility is affected by the strain rate. The strain rates normally used are 0.002 to 0.005 mm/mm/min. in the elastic range of 0.2% offset yield strength and 0.02 to 0.05 mm/mm/min. from that point to failure.^(9, 10)

Maximum tensile strength and minimum acceptable elongation have to be specified to obtain material with maximum formability. Maximum tensile strength ensures that the material will not be excessively cold worked; minimum elongation ensures some ductility under slow (tensile test) strain rates. Increasing amounts of cold working, while promoting bendability, also promote a tendency for delamination, one of the principal causes of part rejection. This has been substantiated by measurements of short-transverse tensile strength made by brazing disks of the sheet into the centers of round tensile specimens. These tests showed that through-the-sheet strength decreased with increasing cold working. Also, excessively cold-worked material appeared undesirable because of decreased recrystallization temperature.⁽³⁾ The specifications for TZM for the X-20 program specified that three sheets per TZM lot were to be tested for transverse tensile properties (ultimate, yield, and elongation) as follows: over 0.5 mm (0.020 inch) thick, 985 MPa (143 ksi) maximum, 911 MPa (135 ksi) maximum, and 7% in 5.04 cm (2 inches) minimum; 0.5 mm (0.020 inch) thick and under - 1034 MPa (150 ksi) maximum, 965 MPa (140 ksi) maximum, and 7% in 5.04 cm (2 inches) minimum.⁽³⁾

These mechanical properties are in agreement with those of McDonnell MMS 184 shown in Appendix A.

1.3.2 Bend Tests - Bend tests are generally conducted to determine the ductile-to-brittle transition temperature or to indicate if the material has reasonable formability. It will yield the minimum bend data and the amount of springback which occurs during bending. The minimum width of the specimens should be 12.7 mm (0.50 inch) or 10 to 12 times the specimen thickness. Punch or ram rates of 2.5 to 25.4 cm (1 to 10 inches) per minute have been used. Because the ram rate has an effect on the test results, the punch or ram rate should be specified in the results.⁽⁹⁾ The National Materials Advisory Board Report MAB-192M specifies a ram rate of 2.54 cm (1 inch) per minute.

Bend tests of the Mo-0.5% Ti sheets for the X-20 program were conducted to determine the brittle-ductile-bend-transition temperature inasmuch as almost all of the sheet passed room-temperature bend tests. The majority (80%) of the sheets showed below -17°C (0°F) transition temperatures. However, increasing the strain rate and size of the specimens to more nearly approximate part fabrication procedures resulted in 62% of the material having a bend transition above room temperature. As a result, the specification was amended to require flanging the full length of both sides of every sheet. Flanges were formed to an angle of 90 degrees over a 2.5t radius at a temperature not to exceed 37°C (100°F) using a mechanical brake press with a peak ram rate of not less than 3.1 m (10 feet) per minute. The flanges were formed in opposite directions on the two sides of the sheet. Later, as the quality of the sheet improved, a sampling plan was authorized for selective checking of sheets 1.5 mm (0.060 inch) and under; each sheet over 1.5 mm (0.060 inch) thick was sampled using bend-test strips.⁽³⁾

McDonnell states that for TZM the less than 1.5 mm (.060 inch) thick the transition temperature shall not exceed 0°C as determined by bending through a 105° angle over a 2T radius at a rate not less than 25.4 cm (10 inches) per minute (Appendix A).

1.3.3 Metallographic Examination - Metallographic examination is used to determine the grain size, and the amount of recrystallization that may be present.

For the X-20 program two factors were considered with regard to recrystallization: the amount in the as-received stress-relieved sheet and the temperature at which it would occur during subsequent processing. The amount permitted in the stress-relieved sheet was set at 15 percent. This was based on sheet impact-test results, which showed that whereas 100 percent recrystallized sheet was brittle, 15 and 50 percent recrystallization was allowable after 1 hour at 1176 to 1204°C (2150 to 2200°F) in vacuum. This restriction also served as an indirect control on the amount of cold work in the sheet.⁽³⁾

Stress relief was called for, but not specified quantitatively in procurement specifications.⁽³⁾

McDonnell included representative microstructures in its MMS 184 (Appendix A) to exhibit acceptable levels of recrystallization.

2.0 BLANKING

Because molybdenum and molybdenum alloys supplied in the stress-relieved condition have internal residual stresses, standard techniques such as shearing and punching tend to produce edge delaminations - even when heat is applied. The removal of edge delaminations and excessive burrs can be time consuming because much careful handwork is required as discussed in the next section. If the delaminations are not removed, they can cause fracture and/or propagate during forming. To avoid this expense, the following techniques are recommended for use on molybdenum. Of these techniques, electrical discharge blanking provides the best edge (freedom from delamination and burrs) but can be more costly.

2.1 Sawing

Molybdenum can be sawed with high-speed-steel band or hacksaws using the practice similar to that normally used for superalloys; no coolant is necessary. Hand hacksawing is suitable for light gages only. On power hacksaws, cutting rates are about 80 strokes per minute at 0.1 mm (0.004 inch) per stroke feed. On bandsaw equipment, 305 m/min (100 fpm) with a 2.4 tooth per cm (6-tooth per inch) blade at pressure setting of 2 1/2 have been recommended. About 3.17 mm (1/8 inch) is generally allowed for the kerf and 4.77 mm (3/16 inch) for camber on sections thicker than approximately 1.5 mm (0.060 inch).⁽¹¹⁾ These bandsaw practices differ in the tooth pitch and blade speeds from those recommended in the TZM sheet evaluation program which follows.⁽¹²⁾ Because the following data is more recent it should probably be more representative of applicable procedures on present material.

Good backup around the saw blade together with a smooth weld joint in the blade is essential to minimize the edge burr or roll over on the molybdenum detail being blanked. A backup of mild steel was found to be satisfactory. All regular sawing can be accomplished on a band saw, including both straight and irregular cuts. Recommended cutting speeds for a Do All saw equipped with a blade having 12.6 teeth per cm (32 teeth per inch) were 91.5 m/min (300 surface feet per minute, sfpm) when sawing .4 mm (0.016 inch) thick TZM, 76.2 m/min or 1.5 mm (250 sfpm) when sawing .5 mm (0.020 inch) thick TZM and 36.6 m/min (120 sfpm) when sawing 1.0 (0.040 or 0.060 inch) thick TZM. When the saw speed was reduced to 15.2 m/min (50 sfpm) during cutting 1.0 and 1.5 mm (0.040 and 0.060 inch) thick TZM, a rough cut was

obtained and the saw teeth started breaking from the blade. Saw speeds of 61 m/min. and 91 m/min. (200 and 300 sfpm) result in rapid blade dulling and may require a blade change after 50 cm (20 inches) of cutting.⁽¹²⁾

2.2 Abrasive Cutting

Abrasive cutting is preferred over sawing or shearing when possible. Abrasive cutting is useful when a smoother cut is desired than can be obtained with band sawing (250 vs. 63 roughness height reading, rhr). Its limitations are slower cutting speeds and the fact that only straight cuts can be obtained.^(13, 14) Cutting speeds of 1.8 m/min. (6 fpm) and 3.6 m/min. (12 fpm) were recommended for 1.5 and .4 mm (0.060 and 0.016 inch) thick TZM material, respectively. A 66 cm (26 inch) diameter aluminum oxide wheel run wet at a constant speed of 1400 rpm was used for these tests. A light burr remained on both the top and bottom surface after abrasive cutting.⁽¹²⁾ Cutoff wheels recommended by manufacturers are A60-N6-RR (wet) by Carborundum, A601-N6R-50 with F sides by Norton, and A46-R-R6 by Simonds.⁽¹¹⁾

2.3 Shearing, Slitting and Punching

Shearing, slitting and punching tend to produce edge delaminations and cracking in the sheet material. However, these operations can be performed satisfactorily provided the shearing dies are kept sharp and the sheet is heated to the proper temperature as shown in Figure I-5.^(11, 15) These operations can be performed at room temperature for 0.5 mm (0.020 inch) and thinner; while heavier gages should be heated as recommended in Figure I-5. It is good practice to keep the dies and tools warm with infrared lamps or strip heaters. For sheets greater than 1.5 mm (0.050 inch) thick an excess of 1.6 to 3.2 mm (1/16 to 1/8 inch) is left for edge grinding or belt sanding in order to remove edge delaminations.^(11, 13, 16, 17)

Sections over about 9.5 mm (3/8 inch) thickness or diameter should be edge machined on a shaper or milling machine rather than sheared. Machining should be done along the edge rather than across to prevent delaminating the edges. It may be desirable to hold the work-piece between steel plates during the machining to avoid chipping the edges.

FIGURE I-5. RECOMMENDED TEMPERATURES FOR SHEARING OR PUNCHING (11, 15)

2.4 Blanking Parts by Chemical Milling

Blanking of molybdenum parts by chem-milling can be accomplished using either nitric-hydrofluoric-chromic acid solution, a nitric-hydrochloric-phosphoric acid solution, or a nitric-sulfuric acid solution. Chemical blanking can be accomplished from both sides simultaneously. Metal removal rates are approximately .025 mm (0.001 inch) per minute from each surface.

The maskants used may be those used for stainless steel/or nickel base alloys such as styrene butadiene elastomers. A photosensitive maskant may also be used. The maximum gage that can be chemically blanked is a function of the maskant thickness and the maskant resistance to the etchant. The use of photosensitive mask permits closer chem-milling tolerances, but is limited to sheets up to 1.5 mm (0.060 inch) thick. Masking with maskants used for steel or nickel is not limited by the material thickness and usual chem-milling tolerances can be obtained. Either method can be successfully used and the choice must be based upon the material thickness, the required tolerances, number of parts to make, and economy.⁽¹⁸⁾

More specific details for chem-milling are described in Section 4.

2.5 Electrical Discharge Blanking (ELOX)

Elox blanking tends to be faster and capable of producing better edges than those presently obtained on chemically blanked parts. Electrical discharge machining requires a dielectric gap between the electrode and work piece. To provide the required gap during machining, the Elox equipment is designed to automatically vary the advance of the electrode (or die) into the work piece, depending upon the current being passed through the work gap. The edge conditions produced by Elox blanking as compared to chemical blanking is shown in Figure I-6.

75X

Chemical Blanked Edge Cross-Section TZM

75X

ELOX Blanked Edge Cross-Section TZM

FIGURE I-6. PHOTOMICROGRAPHS SHOWING EDGE CONDITION PRODUCED
BY CHEMICAL AND ELOX BLANKING

3.0 EDGE PREPARATION

Burrs from previous operations must be removed and edges broken. Also, because of the tendency of molybdenum and its alloys to delaminate during blanking operations such as shearing, sawing or punching, it is necessary to remove all edge delaminations prior to additional processing. If the delaminations are present during subsequent operations, such as forming, the probability is great that the material will fracture during processing. The edge preparation itself may produce delaminations, if improperly performed. The following practices are recommended to remove delaminations or burrs and to radius edges as required after machining operations.

3.1 Hand Finishing

In removing material from part edges by belt sanding, extreme caution must be exercised to prevent vibration during metal removal. This is not a recommended method for rounding the edges. The edges may be rounded by filing and/or finished on a grooved, rubber bonded, abrasive wheel. See Figure 1-7 for recommended procedures.

3.2 Electrochemical Deburring

Hand finishing of molybdenum parts to produce the required edge finish/contour or radius can be very costly. (A radius is primarily important for subsequent diffusion coating.) An electrochemical deburring procedure was developed to minimize potential edge delamination in the TZM sheet and reduce the number of manhours required for hand finishing. Electrochemical deburring removes the chemically blanked "knife edge" and can partially radius the edges by metal removal. This is accomplished by using a DC current 1.24 amps/cm^2 (8 amps/in^2) and a 25% nitric acid solution at 51°C (125°F) as an electrolyte. The part is kept in the solution for 15 minutes and then subjected to a sulfuric-chromic acid desmutting operation. The edge produced by the combination of Elox blanking and electrochemical deburring is satisfactory unless an oxidation protective coating is required in which case further radiusing may be necessary.

DO'S

ABRASIVE MOVING UNDER LIGHT PRESSURE ALONG SHEET EDGE WILL NOT PRODUCE DELAMINATIONS.

DON'TS

ABRASIVE MOVING ACROSS SHEET EDGE WILL PRODUCE EDGE DELAMINATIONS.

Edge Finishing by Belt Sanding

A FINE TOOTH FILE MOVED LIGHTLY ALONG EDGE AS SHOWN WILL CUT SATISFACTORILY.

FILING ACROSS THE SHEET EDGE WILL PRODUCE DELAMINATIONS.

Edge Finishing by Hand Filing

ABRASIVE MOVING UNDER LIGHT PRESSURE ALONG SHEET EDGE WILL NOT PRODUCE DELAMINATIONS.

ABRASIVE MOVING ACROSS SHEET EDGE WILL PRODUCE DELAMINATIONS.

Edge Finishing With Grooved Abrasive Wheel

FIGURE I-7 EDGE PREPARATION TECHNIQUES

3.3 Vibration Deburring For Meeting Coating Requirements

Vibration deburring has been conducted on rather small parts. An example of such a process follows. Small parts, not to exceed 15x15 cm (6x6 inches), and gage thickness of .38 to .76 mm (0.015 to 0.030 inch), can be placed in a vibrator machine such as Supersheen Model No. VT75 using No. 3 aluminum oxide chips, water, and tumbling compound such as VANTROL No. 95. After vibrating the parts for approximately 12 to 18 hours, these thin gage materials required only slight hand working with a rubber bonded abrasive wheel to produce the desired edge finish for the protective coating process. Parts of gage thickness greater than .76 mm (0.030 inch) require considerable hand working to produce satisfactory edges for coating.⁽¹⁸⁾

4.0 MACHINING

Molybdenum and its alloys are more difficult to machine compared with the more familiar structural materials. When machined, molybdenum produces a crumbling chip similar to hardened 1040 steel. Machining practices, in general, are similar for both arc-cast and powder metallurgy materials. The arc-cast material is considered by some to be superior in certain respects because it does not spall or crack as easily and also a better surface finish is obtained. The selection of the machining conditions is critical as small variations in cutting feed and speed may make the difference between success and part breakage. The equipment and tooling must be rigid during the machining operation to avoid delamination due to vibration or flexing. For example, stub length cutters are recommended whenever possible to minimize tool deflection.

The main property of pure molybdenum which has an influence on its machinability is its grain structure. Best machinability is found with the uniform fine fibrous grain produced with normal amounts of working. The hardness of pure molybdenum for this condition is 200/250 Brinell. Recrystallized, or sintered and unworked molybdenum is softer, but difficulties may be encountered in producing a good machined finish. Alloys with small amounts of alloying constituents (Mo-0.5Ti and TZM) machine similar to unalloyed molybdenum having the same microstructure although the tools may wear faster.

If molybdenum has been highly stressed by prior working, stress relieving is recommended to avoid cracking or distortion when machining relieves these stresses nonuniformly. When heavy roughing cuts are taken, stress relieving may be desirable before finish machining.

The choice between high-speed steel and sintered carbide cutting tools depends largely on production quantities. In either case, tool life is shorter than would be expected with steel because molybdenum is considerably more abrasive than steel at the same hardness. High-speed steels are generally used for small quantities or for roughing cuts on

uneven surfaces. The preferred carbide grades are the straight tungsten-carbide-cobalt types recommended for cast iron. Tool angles and rakes are usually similar to those used for cast iron. Work should be firmly chucked; tools, sharp and well supported; machines, rigid and free from backlash.

Many types of machining are done without lubrication. When a lubricant is used, various highly chlorinated oils have proved satisfactory. One cutting fluid that has been widely used consists of approximately a 50:50 mixture of chlorinated oil and trichloroethylene or trichloroethane. Good results have also been reported for sulfur-base cutting oils, but they cannot be used in machining electronic parts because of their deleterious effect on final properties. The reason for sulfur-base cutting oils being unacceptable for electronic parts is uncertain and use of this type of oil is not recommended.

Data on machining refractory alloys has been taken from the Machining Data Handbook compiled by the Machinability Data Center, 1972, by permission of Metcut Research Associates Inc., Cincinnati, Ohio.

4.1 Face Milling

When face milling molybdenum, there are two primary origins of damage to the work-piece; fracture at the point of cutting tool impact and chipping at the line of tool exit. Fracture at tool impact can be minimized by rigid tooling and part support in the direction of impact and cutting forces. Chipping at tool exit can be avoided by such methods as chamfering the area, minimizing chip thickness, and by using rigid work back-ups. Climb milling should always be used.^(3, 21)

Negative rake angle cutters should not be used, because molybdenum tends to chip out during milling, producing a poor surface finish. Surface finishes of 3.175 to 5.08 microns (125 to 200 microinches) have been reported⁽²²⁾ with 0° axial rake and 0° radial rake carbide cutters, whereas surface finishes poorer than 8.89 microns (350 microinches) were observed when negative rake cutters were used. Negative rake angles also result in decreased tool life.⁽¹⁹⁾

Both a soluble oil (1:20) or a highly chlorinated oil are indicated to be far superior to face milling dry with carbide cutters. (19, 22)

Basic milling recommendations are presented in Table I-1. (23)

4.2 End Milling

End milling can be performed using standard high speed steel tools. Tool life can be increased by using shorter-than-standard end mills, to improve the rigidity of the setup and by increasing the clearance angle of the tools to 10° to 12°. Relatively high feed rates should be used. The cutters will wear rapidly if too low a feed rate is used or if the cutter is allowed to dwell in the cut. The cutting speed for peripheral end milling should be greater than that for slot end milling. There is no concise agreement as to the best cutting fluid; a soluble oil is a good general purpose fluid for machining molybdenum.

The basic milling recommendations are presented in Table I-2. (23)

4.3 Side and Slot Milling - Arbor Mounted

The basic recommendations for side and slot milling are presented in Table I-3. (23) The recommended cutting fluids, when using high speed steel tools, are either heavy duty oil or heavy duty soluble oil. When using carbide tools, the recommended fluids are either medium duty oil or heavy duty soluble oil.

4.4 Turning

Various tool geometries and materials have been used successfully. High speed steel tools may be used for rough turning; however, the cutting force will be larger, tool life shorter, and surface finish poorer than for the same cut using carbide tools. (21) A large positive side rake angle on the tool has proved to be very beneficial in successful turning of molybdenum and its alloys. Small nose radii and sizeable side relief angles are advised. A soluble oil works very satisfactory as a cutting fluid. (16, 17, 19, 21, 22, 24, 25)

TABLE I-1. FACE MILLING RECOMMENDATIONS (23)

SPEEDS AND FEEDS

MATERIAL	HARDNESS BHN	CONDITION	DEPTH* OF CUT mm (inches)	HIGH SPEED STEEL TOOL			CARBIDE TOOL			
				SPEED m/min (fpm)	FEED mm/tooth (in./tooth)	TOOL MATERIAL	SPEED m/min(fpm)		FEED mm/tooth (in./tooth)	TOOL MATERIAL
							BRAZED	THROW- AWAY		
Molybdenum TZM	220 to 290	Stress Relieved	2.5 (.100)	27.4 (90)	0.25 (.010)	T15, M33, M41 Thru M47	68.6 (225)	76.2 (250)	0.12 (.005)	C-2
			0.38 (.015)	36.6 (120)	0.20 (.008)	T15, M33 M41 Thru M47	77.7 (255)	83.8 (275)	0.10 (.004)	C-2

*Depth of cut is measured parallel to axis of cutter.

**Due to the brittleness of refractory alloys, cracking, chipping, flaking and breakout tend to occur, particularly on the edges of the machined surfaces.

TOOL GEOMETRY

HIGH SPEED STEEL		THROWAWAY CARBIDE		BRAZED CARBIDE		CORNER ANGLE degrees	END CUTTING EDGE ANGLE degrees	AXIAL RELIEF ANGLE degrees	RADIAL RELIEF ANGLE degrees
AXIAL RAKE ANGLE degrees	RADIAL RAKE ANGLE degrees	AXIAL RAKE ANGLE degrees	RADIAL RAKE ANGLE degrees	AXIAL RAKE ANGLE degrees	RADIAL RAKE ANGLE degrees				
0	20	5 to 7	0 to 5	0	0	45	5 to 10	10	10

TABLE I-2. END MILLING RECOMMENDATIONS FOR MOLYBDENUM

SPEEDS AND FEEDS**End Milling-Peripheral**

HARD- NESS BHN	CONDITION	DEPTH OF CUT mm (inches)	HIGH SPEED STEEL TOOL						CARBIDE TOOL					
			SPEED m/min (fpm)	FEED ~ mm(inches) per Tooth				TOOL MTL	SPEED m/min (fpm)	FEED ~ mm (inches) per Tooth				TOOL MTL
				CUTTER DIAMETER mm (inches)						CUTTER DIAMETER mm (inches)				
				6.35 (1/4)	12.7 (1/2)	19.05 (3/4)	25 to 50 (1 to 2)			6.35 (1/4)	12.7 (1/2)	19.05 (3/4)	25 to 50 (1 to 2)	
220 to 290	Stress Relieved	1.27 (.050)	51.8 (170)	.050 (.002)	.075 (.003)	.10 (.004)	.10 (.004)	T15*	91.4 (300)	.050 (.002)	.075 (.003)	.10 (.004)	.100 (.004)	C-2
		.38 (.015)	60.7 (200)	.038 (.0015)	.050 (.002)	.038 (.0015)	.050 (.002)	T15*	99.1 (325)	.025 (.001)	.025 (.001)	.038 (.0015)	.050 (.002)	C-2

End Milling-Slotting

HARDNESS BHN	CONDITION	DEPTH* OF CUT mm (inches)	SPEED m/min (fpm)	FEED – mm (inches) per Revolution				HSS TOOL MATERIAL except as noted
				NOMINAL HOLE DIAMETER – mm (inches)				
				6.35 (1/4)	12.7 (1/2)	19.05 (3/4)	25 to 50 (1 to 2)	
220 to 290	Stress Relieved	6.35 (.250)	32.0 (105)	—	—	.050 (.002)	.075 (.003)	T15, M33, M41 Thru M47
		1.27 (.050)	35.1 (115)	.018 (.0007)	.025 (.001)	.038 (.0015)	.050 (.002)	

TOOL GEOMETRY

HARDNESS BHN	HELIX ANGLE degrees	RADIAL RAKE ANGLE degrees	END CUTTING EDGE CONCAVITY ANGLE degrees	AXIAL RELIEF ANGLE degrees	RADIAL† RELIEF ANGLE degrees
170-290	30	10	3 to 7	3 to 7	C

†Radial Relief Angles for Various Size End Mills:

Size*	3.18 (1/8)	4.76 (3/16)	6.35 (1/4)	9.52 (3/8)	12.7 (1/2)	19.05 (3/4)	25.4 (1)	38.1 (1-1/2)
C	19	19	15	13	13	12	10	8

*UNITS - mm (in.)

TABLE I-3. SIDE AND SLOT MILLING RECOMMENDATIONS FOR MOLYBDENUM. (ARBOR MOUNTED CUTTERS).

SPEEDS AND FEEDS

HARDNESS BHN	CONDITION	DEPTH* OF CUT mm (inches)	HIGH SPEED STEEL TOOL			CARBIDE TOOL		
			SPEED m/min (fpm)	FEED mm/tooth (in./tooth)	TOOL MATERIAL	SPEED m/min (fpm)	FEED mm/tooth (in./tooth)	TOOL MATERIAL
220 to 290	Stress Relieved	6.35 (.250)	30.5 (100)	.127 (.005)	T15, M33, M41 Thru M47	53.3 (175)	.178 (.007)	C-2
		1.27 (.050)	35.1 (115)	.178 (.007)	T15, M33, M41 Thru M47	61.0 (200)	.229 (.009)	C-2

TOOL GEOMETRY

HARDNESS BHN	HIGH SPEED STEEL				CARBIDE			
	AXIAL RAKE ANGLE degrees	RADIAL RAKE ANGLE degrees	AXIAL RELIEF ANGLE degrees	RADIAL RELIEF ANGLE degrees	AXIAL RAKE ANGLE degrees	RADIAL RAKE ANGLE degrees	AXIAL RELIEF ANGLE degrees	RADIAL RELIEF ANGLE degrees
170-290	0	15 to 20	3 to 5	5 to 10	0	5 to 15	7 to 10	7 to 10

The metal removal rates are comparable to those of nickel and cobalt base superalloys, and as fast or faster than those of martensitic steels heat treated to 1861 to 2069 MPa (270,000 to 300,000 psi).

The basic recommendations for turning are presented in Table I-4.

4.5 Drilling

Molybdenum can be drilled with very little difficulty using high speed steel drills and standard equipment and procedures.

As in other machining operations, success depends upon the rigidity of the setup. For this reason more difficulty can be expected when using portable drilling methods or when drilling small holes.

The major potential difficulty may be part fracture during drill breakthrough. Holes perpendicular to the fiber of wrought parts may open transverse cracks. This potential damage can be alleviated if the part has sufficient backup or is heated above the ductile-to-brittle transition temperature. (3, 11, 12, 20, 21, 22, 24, 26)

The standard 118° point chisel-edge drill performs well from a tool life standpoint. Other considerations such as axial thrust requirements, which when decreased also decrease the probability of part fracture during breakthrough, may warrant using a split-point geometry with 135° point angle. Drill speeds of 9.14 to 38.1 m/min. (30 to 125 ft/min.) with a feed rate of .076 to .254 mm (0.003 to 0.010 in/rev.) has provided satisfactory holes. (12, 19, 21, 22, 25)

The use of carbide drills is recommended for drilling very deep holes (more than 3 times hole diameter) because of abrasive molybdenum chips.

Other precautions that may be necessary, because of the molybdenum chips, are using carbide wear strips along the shank, relieving the drill, feeding the drill from below or using a pressurized coolant. (11, 24)

TABLE I-4. TURNING RECOMMENDATIONS FOR MOLYBDENUM.
(SINGLE POINT AND BOX)

SPEEDS AND FEEDS

HARDNESS BHN	CONDITION	DEPTH* OF CUT mm (inches)	CARBIDE TOOL			
			SPEED - m/min (fpm)		FEED mm/rev (ipr)	TOOL MATERIAL
			BRAZED	THROW- AWAY		
220 to 290	Stress Relieved	2.54 (.100)	88.4 (290)	—	.25 (.010)	C-2
		.38 (.015)	99.1 (325)	—	.127 (.005)	C-2

TOOL GEOMETRY

NOTE: ALL RAKE AND RELIEF ANGLES ARE
MEASURED IN NORMAL DIRECTION.

HARDNESS BHN	HIGH SPEED STEEL AND CAST ALLOY TOOL					CARBIDE TOOLS						
	BACK RAKE ANGLE degrees	SIDE RAKE ANGLE degrees	END RELIEF ANGLE degrees	SIDE RELIEF ANGLE degrees	SIDE AND END CUTTING EDGE ANGLE degrees	BRAZED		THROWAWAY		END RELIEF ANGLE degrees	SIDE RELIEF ANGLE degrees	SIDE AND END CUTTING EDGE ANGLE degrees
						BACK RAKE ANGLE degrees	SIDE RAKE ANGLE degrees	BACK RAKE ANGLE degrees	SIDE RAKE ANGLE degrees			
170-290	0	20	5	5	5	0	20	-	-	5	5	15

Since the coefficient of thermal expansion of molybdenum is considerably less than that of steel, it is necessary to use copious amounts of coolant to prevent seizing of the drill and possible fracture of the workpiece. A highly chlorinated oil appears to have slight advantages over soluble oils for drilling. (4, 11, 17, 20, 21, 22, 24, 26)

The basic recommendations for drilling are presented in Table I-5.

4.6 Grinding

Grinding of molybdenum and its alloys can be accomplished. However, it can be difficult and expensive because the wheels tend to load rapidly and require frequent dressing. Severe chatter occurs when a loaded wheel is used. The work should be oriented so that the axis of the wheel is perpendicular to the plane of the sheet to prevent delamination of the workpiece edges. (3) It has been stated (21) that the process should be considered primarily for achieving dimensional accuracy rather than stock removal, or to a lesser extent to achieve a desired surface finish. Surface finish measurements in the range of .25 to .89 microns (10 to 35 microinches) can be obtained depending upon the grinding conditions. The types of abrasive wheels and fluids have a major effect on performance during grinding. (19, 21, 22)

Aluminum oxide has proved to be a very satisfactory abrasive material. As might be expected, larger grit wheels generally perform better, except for surface finish, because they tend to load up less. (21, 24)

(11) Grinding wheels recommended by several manufacturers are listed below:

	<u>Carborundum</u>	<u>Norton</u>	<u>Simonds</u>
Surface Grinding	AA60-H8-V40 (dry) GA60-J8-V40 (wet) AA100-I5-V40 (dry, form)	32A60-G12VBEP (dry) 19A46-J5VG (wet)	SA60-H16-V (dry) NA46-I8-V1 (wet)
Cylindrical Grinding	DA465-K6-V11 (wet, roughing) DA80-K6-V11 (wet, finishing)	19A60-L5VG (wet)	A60-K5-V1

TABLE I-5. DRILLING RECOMMENDATIONS FOR
MOLYBDENUM

SPEEDS AND FEEDS

HARDNESS BHN	CONDITION	SPEED m/min (fpm)	FEED – mm (inches) per Revolution				HSS TOOL MATERIAL except as noted
			NOMINAL HOLE DIAMETER – mm (inches)				
			1.58 (1/16)	3.17 (1/8)	6.35 (1/4)	12.70 (1/2)	
220 to 290	Stress Relieved	22.9 (75) 33.5 (110)	.025 (.001) –	.075 (.003)	.127 (.005)	.177 (.007)	T15, M33, M41 Thru M47

TOOL GEOMETRY

High Speed Steel Twist

HARDNESS BHN	POINT ANGLE degrees	LIP RELIEF ANGLE degrees	CHISEL EDGE ANGLE degrees	HELIX ANGLE degrees	POINT GRIND
170-290	118	7 to 10	125 to 135	24 to 32	Standard

The best surface grinding efficiency is achieved at wheel peripheral speeds of 915 to 1220 m/min. (3000 to 4000 ft/minute), which is below the design speed of many machine shop tools.⁽²¹⁾ The wheel downfeed is limited to approximately .025 mm (0.001 inch)/pass because of increased likelihood of workpiece damage if a larger downfeed is used.^(11, 21, 22, 24) Figure I-8 shows the effects of grinding parameters on the metal removal rate of pure molybdenum and Mo-0.5 Ti alloy.

A water soluble oil is a satisfactory coolant for grinding. A solution of 5 to 20 percent potassium nitrite has been reported to improve grinding efficiency, at least for TZM alloy. If insufficient cooling is used, heat checking may occur which will lead to surface cracking.^(19, 21, 22)

The basic grinding recommendations are presented in Table I-6.

TABLE I-6. GRINDING RECOMMENDATIONS FOR MOLYBDENUM
(HORIZONTAL SPINDLE, RECIPROCATING TABLE)

HARDNESS BHN	CONDITION	WHEEL SPEED m/min (fpm)	TABLE SPEED m/min (fpm)	DOWNFEED mm/pass (in./pass)	CROSSFEED mm/pass (in./pass)	WHEEL
220 to 290	Stress Relieved	1219 (4000)	12.2 to 24.4 (40 to 80)	Rough .025 (.001) Finish .0127 (.0005) max.	.050-5.08 (.020-.200) (Max: 1/12 of Wheel Width)	A46JV

4.7 Chemical Milling

Chemical milling has been used as both a blanking and metal removal process. Chemical milling can be accomplished using either a nitric-hydrofluoric-chromic acid solution, a nitric-hydrochloric-phosphoric acid solution, a nitric-sulfuric acid solution, or a nitric-hydrofluoric acid solution. Metal removal rates are approximately .025 mm (0.001 inch) per minute from each surface, dependent upon solution freshness and temperature. The maskants used may be those used for stainless steel or nickel base alloys, such as styrene butadiene elastomers.^(16, 23, 25)

CONSTANT GRINDING CONDITIONS

WHEEL GRADE: A46H8U
DOWNFEED: .025mm(0.001 IN.)/PASS
GRINDING FLUID: SOLUBLE OIL, 2-1/2

BASIC VARIABLE TEST PARAMETERS

WHEEL SPEED: 1220 m (4000 FT)/MIN
CROSS FEED: .127 mm (0.005 IN.)/PASS
TABLE SPEED: 12.19 m (40 FT)/MIN

FIGURE I-8. COMPARISON OF SURFACE GRINDING CHARACTERISTICS OF 2 MOLYBDENUM COMPOSITIONS (21)

A 45% HNO_3 + 3.5% HF + H_2O solution at 43°C (110°F) has been used successfully at McDonnell. The parts should be racked in a plastic container and dipped into an agitated chem mill tank. After half the required etching time the container should be removed, the parts rinsed in cold water, and rotated top for bottom. Immerse the container back into the solution until the chem-milling is completed, rinse in cold water, place parts in a desmutting solution, 11.3% H_2SO_4 + 20.4 gm/1000cc (.17 lb/gal) chromic acid + water at ambient temperature, until all smut is removed. Rinse in cold water and dry.

No specific information was found on tolerances or surface finishes that could be expected on molybdenum and its alloys. General tolerances are probably $\pm .15$ to $.30$ mm (.006 to .012 inch) for a 1.5 mm (.060 inch) sheet. The tolerance that is obtained depends upon the complexity of part configuration; the etchant type, temperature and condition; and the etch time. Surface finishes of 50 RHR on tungsten sheet is considered average. Using this as a guide, one could expect a similar finish on molybdenum. ⁽²³⁾

5.0 FORMING

Forming processes used for molybdenum and TZM are sensitive to the peculiar characteristics caused by the prior processing history.

General characteristics to be considered during forming operations are:

- ° The amount of warm working done below the recrystallization temperature effects the yield strength and ductility of molybdenum and therefore the amount of forming that can be performed without fracture. Too little warm work results in poor mechanical properties and a high ductile-to-brittle transition temperature. Too much work may eliminate material for a particular forming operation because of reduced ductility. Unalloyed molybdenum should receive approximately 50 to 60 percent reduction in area for good formability. Because of the limited ductility of molybdenum and its alloys, forming procedures are very important. Procedures must be adapted to optimize performance for each operation and then carefully controlled.

- ° Fully recrystallized molybdenum has poor bend and impact characteristics, even though the tensile elongation is higher than in other conditions. For this reason, fully recrystallized molybdenum is not recommended.

- ° The toughness and ductility of molybdenum are significantly higher at temperatures above the ductile-to-brittle transition temperature (DBTT). A moderate amount of heat is recommended for all working operations to minimize the possibility of cracking during forming. Methods and amounts of heating will be discussed later.

- ° Molybdenum heats and cools rapidly because of its high thermal conductivity and low specific heat. For this reason, continuous heating of the workpiece must be performed for many operations.

- ° At elevated temperatures molybdenum possesses high strength and therefore more powerful equipment is generally needed to perform an equal amount of work on a lower strength material such as steel.

- ° The surface condition of the molybdenum should be free of stress risers which could generate cracks during forming. Figure I-9 shows that .1 mm (0.004 inch) removed from 1.6 mm (1/16 inch) thick sheet by chem-milling improved the formability significantly.⁽¹²⁾

FIGURE I-9. EFFECT OF CHEMICAL MILLING ON BEND TEST RESULTS FOR 1.6MM (1/16 INCH) THICK MOLYBDENUM-BASE ALLOY SHEET-TZM, STRESS RELIEVED

There are certain problems that can be expected when forming molybdenum and its alloys. Perhaps the greatest problem is that of cracking and delamination. These will tend to occur more frequently in cutting, shearing, punching or drilling operations used to prepare blanks. These defects then tend to propagate when the defective area is stressed in a subsequent forming operation. Therefore, extreme importance is placed on the blanking and edge preparation procedure used. (See Sections 2 and 3). Dimensional stability is a minor problem encountered as a result of over or under forming, variable springback, and relief of residual stresses. Under or over forming usually occur because of inadequate tooling. Expensive hardened tools and dies are not usually used if only a limited number of parts are made which does not justify the cost for more elaborate tooling. Caution is required in overforming molybdenum because reverse bending can cause delaminations. Overbends of up to 5° could be reworked without special problems according to Stratton, et al.⁽³⁾ The uniformity of raw stock, both within a single piece and from piece-to-piece, has improved with more experience in primary fabrication and should continue to improve. Dimensional changes during stress relief can present problems when molybdenum is formed at or near room temperature. In some cases, the stress relief may not be completed until after a coating process; thus dimensional changes may occur during a coating process. The dimensions of coated parts often may not be corrected without cracking the coating.^(11, 13, 16, 17, 25, 27, 28, 29)

The relative ease or difficulty with which a part may be fabricated is affected by the basic design of the part. It stands to reason that the designs should be kept as simple as practicable to minimize severe forming requirements.

Theoretical formability limits have been developed by W. W. Wood, et.al^(30, 31). These act as useful guides from both a processing as well as a design standpoint. The details of the curves and equations are too extensive to be included in their entirety in this report, however, key curves are included when practical. The molybdenum used by Wood could be classified as "old" (poorer formability) because the work was done prior to completion of the Bureau of Naval Weapons refractory metals program.

5.1 Heating and Forming

When required heating of molybdenum can be done with propane or acetylene torches, in furnaces, with infrared or quartz lamps, or resistance heaters. Except for small sizes, molybdenum can be heated to about 371°C (700°F) in air without excessive oxidation provided the heating time is not too long. When temperatures greater than 371°C are needed, a controlled atmosphere furnace with a vacuum, inert gas or a slightly reducing atmosphere can be used. Cracked ammonia is not recommended for use at high temperatures because of the deleterious effect of nitrogen on formability. Also a non-oxidizing salt bath may be used for heating.

Precautions should be taken so that the molybdenum does not come in contact with the slag or scale within a furnace. Molybdenum can be placed on a stainless steel plate, but the best practice is to isolate the molybdenum from the iron by placing the molybdenum on molybdenum spacers.

Close temperature control must be maintained so that no portion of the workpiece is overheated and recrystallized. Because of preferential work that occurs in some formed areas, recrystallization may occur if these highly stressed areas are overheated. Optical pyrometers, photocell infrared sensors, contact pyrometers, or temperature indicating crayons may be used for determining the temperatures.

Because molybdenum has high thermal conductivity 146.2 W/m·K (84.5 BTU·ft/hr. sq.ft. °F) it will reach uniform temperatures rapidly. It will require only one-fourth as much time to reach temperature as carbon steels. No hold time is necessary with small workpieces. It should be remembered that molybdenum will also cool rapidly. For this reason it is a good practice to keep the dies and tools warm.

Molybdenum should be heated to the temperature relative to its thickness and the forming speeds used in order to obtain optimum results. The metal should be formed above its DBTT. It is desirable to keep the temperature as low as possible, ideally at room temperature, to minimize oxidation and avoid the loss in ductility that occurs at intermediate elevated temperatures. See Figure I-10. (3, 11, 15, 20, 26, 28, 32)

FIGURE I-10. SPECIFIED FABRICATION TEMPERATURES FOR 1/2 Ti-MOLYBDENUM AND MOLYBDENUM ALLOYS (15) *

* "OLD" MATERIAL

5.2 Brake Forming

Brake forming is the simplest method of forming where sheet metal is bent to form straight sections such as angles, channels and hats. Air and die bending are commonly used. In air bending, the workpiece is supported at its outer edges only and the length of the ram stroke determines the part angle. In die bending, the workpiece is forced into a female die cavity of the required part angle. See Figure I-11.

Bends of 105° have been made on TZM sheet at room temperature using forming rates of 2.54 and 30.48 cm/min. (1 ipm and 12 ipm). For this operation, care must be exercised to remove all edge cracks and delaminations. When the higher forming rates are used, the bend radius must be increased. The following table is a comparison of the 2.54 cm/min. (1 ipm) forming rate (performed on tensile machine) and the 30.48 cm/min. (12 ipm) forming rate (performed on production brake). The bends were in the transverse, longitudinal and 45° directions. For these tests the samples were prepared by blanking with Do All saw followed by smoothing the edges by filing and sanding with #120 grit paper.⁽¹²⁾ ("new" material)

TABLE I-7. TZM ROOM TEMPERATURE BEND TEST RESULTS SUMMARY

	TENSILE MACHINE 2.54 cm/min. (1 ipm)				PRODUCTION BRAKE 30.48 cm/min. (12 ipm)			
	1.5 (0.060)*	1.0 (0.040)	.50 (0.020)	.40 (0.016)	1.5 (0.060)	1.0 (0.040)	.50 (0.020)	.40 (0.016)
Longitudinal	1T	1T	1T	1T	2T	2T	1T	1T
45°	2T	2T	1T	1T	4T	3T	3T	3T
Transverse	2T	2T	2T	2T	4T	3T	3T	3T
*mm (inches)								

One "T" bends were accomplished on .40 mm (.016 inch) and 1.5 mm (0.060 inch) thick material at 2.54 cm/min. (1 ipm) on a tensile machine at a temperature of 148°C (300°F).⁽¹²⁾

The brake forming temperature required by Boeing⁽³⁾ is 148°C (300°F). They recommended tool temperatures of 148 $\pm$ 111°C (300 $\pm$ 200°F) and a part preheat temperature of 260 $\pm$ 55°C (500 $\pm$ 100°F) with a delay time of 15 seconds. Thin gage (12) less than .5 mm (.020 inch) material can sometimes be formed at room temperature. The optimum forming temperatures for brake forming as reported by Wood⁽³⁰⁾ are shown in Figure I-12.

FIGURE I-11. BENDING PROCESSES

FIGURE I-12. OPTIMUM FORMING TEMPERATURE CURVES FOR: BRAKE FORMING.

The forming limit table, Table I-8, to determine theoretical minimum bend radii can be used as follows:

1. Determine the bend angle (α), the material thickness (T), and the direction of bending, i.e., either longitudinal (L) or transverse (T).
2. Compare the bend angle required to the critical bend angle.
Case 1: If the known bend angle is greater than the critical bend angle, then the bending limits are the same as the tabulated critical bending limits.
Case 2: If the known bend angle is less than the critical bend angle, interpolate the tabulated R/T ratios and the various angles (α) below critical to determine the required R/T ratio.
3. Multiply the bending limit (R/T) by the material thickness (T) to determine the minimum radius of bend (R).

The formability envelope is shown in Figure I-13. Theoretically, all formable parts are limited to the area above the curve.

FIGURE I-13. BENDING FORMABILITY ENVELOPE

TABLE I-8. BENDING LIMITS FOR BRAKE FORMING⁽³⁰⁾

MATERIAL	GRAIN DIRECTION	BENDING TEMPERATURE	CRITICAL BEND α°	CRITICAL BEND LIMITS R/T	Bending Limits (R/T)						
					For Various Angles (α) Below Critical						
					30	45	60	75	90	105	120
TZM Moly	L	R.T.	121	1.12	.30	.55	.81	.98	1.10	1.12	1.12
TZM Moly	L	260	118	1.40	.10	.20	.25	.30	.50	1.10	1.40
Cb-752	L	R.T.	121	1.20	.38	.60	.85	1.05	1.18	1.20	1.20
Cb-752	L	260	115	2.00	.15	.20	.40	.75	1.30	1.80	2.00
2024-T3	L	R.T.	111	2.02	.50	.90	1.38	1.70	1.90	2.0	2.0
2024-T3	L	315	122	1.07	.17	.28	.45	.75	1.00	1.15	1.18
PH 15-7 Mo	L	815	126	.65	.05	.08	.12	.20	.38	.55	.63

5.3 Joggling

Procedures have been developed for successfully joggling 0.40 to 1.5 mm (0.016 to 0.060 inch) sheet with a joggle ratio (length to depth) of from 3 to 5. The joggle minimum length to depth ratios are shown in Table I-9. These procedures involve using a two step process. All forming is accomplished at room temperature. Initially the blanks are bent to a 90° angle on a brake press. The balance of the forming can be made with a standard punch press and dies. An overlay of 4130 and/or 321 stainless steel is recommended for use on top of the blanks to set the joggle^(12, 34). ("new" material)

If the material to be formed is not in the optimum condition and failures are encountered, an alternate procedure can be used. This procedure is also a 2 step one but involves preforming the blank at room temperature on a hydropress with hard-lead plates, soft-lead strap, and urethane-rubber overlays ("Guerin Trapped Rubber Process"). These preforms can then be final formed at 76°C (170°F) in a Sheridan Gray Press.

The theoretical limit curve for molybdenum-0.5 Ti proposed by Wood, et. al⁽³¹⁾ is shown in Figure I-14. The plotted points on this curve are from joggles in 1.5 mm (0.060 inch) thick TZM by Jackson⁽¹²⁾ for TZM. These show that TZM performs better than is theoretically proposed for molybdenum-0.5 Ti.

5.4 Corrugation

Corrugations have been formed in .4 mm (0.016 inch) thick cold worked/stress relieved TZM sheet at room temperature. The corrugation configuration had a 20.75 mm (0.817 inch) pitch, 10 mm (0.400 inch) depth, 8 mm (0.320 inch) flat, and 1.5 mm (0.06 inch) bend radius. No difficulties were encountered in forming corrugations in nine 10.2x15.2 cm (4.0x6.0 inch) panels; this involved 72 forming operations. Panels were formed at room temperature with a "V" configuration 9.75 min. (0.384 inch) high, a 2.54 cm (1.00 inch) pitch, and .4 mm (0.016 inch) bend radius. Nine 30.5x45.7 cm (12.0x18.0 inch) panels were formed at room temperature with 23 corrugations per panel with no difficulty. A photograph of the corrugated panels is shown in Figure I-15.⁽¹²⁾ ("new" material)

TABLE I-9. JOGGLE MINIMUM LENGTH TO DEPTH RATIOS FOR TZM

GAUGE*	1.5 (0.060)			1.0 (0.040)			0.5 (0.020)			0.4 (0.016)		
DEPTH* LENGTH*	1.5 (0.060)	3.2 (0.125)	4.7 (0.187)	1.5 (0.060)	3.2 (0.125)	4.7 (0.187)	1.5 (0.060)	3.2 (0.125)	4.7 (0.187)	1.5 (0.060)	3.2 (0.125)	4.7 (0.187)
5.0 (0.200)												
10.2 (0.400)												
12.7 (0.500)												
15.2 (0.600)												
22.9 (0.900)												

*DIMENSION UNITS — mm (in.)

"new" material

FIGURE I-14. COMPARISON OF JOGGLES IN TZM^{*} WITH THEORETICAL LIMIT CURVE FOR JOGGLES IN Mo.-0.5Ti

* "new" material

+ "old" material

FIGURE I-15. 0.4 mm (0.016 inch) TZM CORRUGATED PANELS

5.5 Beading

Beading is one of the most severe of the fabrication processes, but can be accomplished if proper processes are used. Beading of 35.5x63.5 cm (14x25 inch) molybdenum TZM panels has been accomplished with drop hammer forming, provided the elongation was limited to less than 7%. The parts were heated in an air furnace to about 148°C (300°F). Kirksite dies lubricated with Everlube were used. Forming was accomplished with two light strikes followed by a final heavy stroke, using rubber pads to aid in sequencing the depth of forming per strike. The rubber thicknesses used were 12.7 mm (1/2 inch) on the first strike, 6.35 mm (1/4 inch) on the second strike, and no rubber on the final strike. The parts were reheated when the part temperature fell below 121°C (250°F). The beaded panels are shown in Figure I-16.⁽¹²⁾ ("new" material)

The rubber forming beaded panel forming limits derived by Wood, et al, (30) is shown in Table I-10. These limits are based on a 21 MPa (3000 psi) maximum forming pressure. Instructions for using the table are as follows:

- ° Calculate L/T ratio from given dimensions.
- ° Compare the known L/T with the tabulated critical L/T.
 - Case 1: If the known L/T is less than the critical L/T, then the maximum bead radius (R Max.) obtained will be due to insufficient pressure 21 MPa (3000 psi). Interpolate the tabulated L/T values and corresponding R/L values for insufficient pressure to determine the required R/L ratio. Multiply R/L by the distance between bead centers (L) to determine the maximum bead radius (R Max.).
 - Case 2: If the known L/T is greater than the critical L/T, interpolate the tabulated L/T ratios and corresponding R/T values for splitting to determine the required R/T ratio. Multiply R/T by the material thickness (T) to determine the maximum bead radius (R Max.).

The theoretical limit curves for drop hammer beading are presented in Figure I-17.

TRIMMED BUT NOT
PICKLED

TRIMMED, PICKLED
AND ZYGLO
INSPECTED

TRAP NOT
TRIMMED

FIGURE I-16. MOLYBDENUM (TZM) DROP-HAMMER FORMED PANELS

TABLE I-10. RUBBER FORMING BEADED PANEL FORMING LIMITS FOR M0-TZM(30)

Critical Ratio	Insufficient Pressure Limits (R/L)		Splitting Limits (R/T)	
	For R/T Ratios of		For R/L Ratios of	
	Temp.	Temp.	Temp.	Temp.
L/T	°C	°C	°C	°C
154	R.T.	30	.01	.20
	R/L	.162	.03	.10
148	R.T.	143	.06	.40
	R/L	.21	.42	.32
148	538	143	45	400
	L/T	88.3	1500	160

FIGURE I-17. COMPOSITE OF OPTIMUM DROP HAMMER LIMIT CURVES IN THE ROOM TEMPERATURE TO 315°C (600°F) RANGE

5.6 Dimpling

Lamination free dimples on .4 and .5 mm (.016 and .020 inch) thick TZM have been produced on 2.49 to 4.90 mm (.098 to .193 inch) diameter holes. The dimpling was performed at 148°C (300°F) using standard equipment (Chicago Pneumatic Model 450EA). Dimples in mating surfaces also were dimpled simultaneously, which produced a more satisfactory "fit-up". The parameters used for the dimpling are presented in Table I-11.⁽¹²⁾

TABLE I-11. Dimpling Parameters⁽¹²⁾ ("new" material)

Procedure	Hole Temp., (°C)	Dwell Time (Sec)	Coining Raw Pressure MPa (psi)	Dwell Pressure MPa (psi)
Dimpled Simultaneously	149	10	.070 (10)	.525 (75)
Dimpled Separately	149	10	.070 (10)	.280 (40)

Dimpling of Mo-0.5 Ti was reported by Stratton, et al.,⁽³⁾. They required dimpling temperatures of $260 \pm 10^\circ\text{C}$ ($500 \pm 50^\circ\text{F}$); heaters within 6.35 mm (1/4 inch) of the tool face; the ram should be adjusted from 0.000 to .4 mm (0.016 inch) below the tool face depending on gage; dwell times of 4 to 9 seconds; and dwell pressures from .21 to .42 MPa (30 to 60 psi) for gages up to 1.5 mm (0.060 inch). ("old" material)

The theoretical limit curves are presented in Figure I-18.

5.7 Hydroforming

Rubber Forming

A method of die forming sheet metal where rubber is normally used as the female die; principally used for flanging and shallow recessing. There are two process types, single and double action. In the single action process the forming pressure is exerted from only one direction, whereas in the double action process the pressure is applied from two directions. These are shown schematically in Figure I-19.

FIGURE I-18. THEORETICAL DIMPLING LIMIT CURVES

FIGURE I-19. RUBBER DIE FORMING PROCESSES

The rubber forming shrink flange limits (50) are presented in Table I-12. The instructions for using the table are as follows:

- ° Calculate R_D/T ratio from given dimensions.
- ° Compare the known R_D/T with the tabulated critical R_D/T .
 - Case 1: If the known R_D/T is less than the critical R_D/T , multiply K times R_D to determine the maximum flange height (H Mas.).
 - Case 2: If the known R_D/T is greater than the critical R_D/T , interpolate the tabulated R_D/T ratios and corresponding H/T values for buckling to determine the required H/T ratio. Multiply H/T by the material thickness (T) to determine the maximum flange height (H. Max.).
- ° Multiply the pressure limit (H/T) by the material thickness (T) to determine the minimum flange height (H Min.).

The rubber forming stretch flange limits (30) are presented in Table I-13. The instructions for using these are the same as those above. The table indicates that there is little difference in forming characteristics between RT and 260°C (500°F).

To overcome the rigidity of TZM and produce closer adherence to form block contour, lead has been tried as the overlay instead of the rubber. First the flat-patterned TZM was placed on the form block, next a piece of 0.008 aluminum foil to aid in slippage between the lead and TZM, third a piece of antimony alloy hard lead to set the flanges, and finally strips of commercially pure lead to hold the hard lead which cracked during the forming operation. Figure I-20 shows the specimen on the form block before and after forming, using the lead back-up.⁽¹²⁾ ("new" material)

In general, the 0.2 mm (0.008 inch) aluminum foil is required when forming the heavier gauge TZM with a lead overlay. Figure I-21 shows a part formed with and without the aluminum foil. The thinner gauge material can be formed without fracture by using either the lead or rubber overlay. Smaller wrinkles did occur, however, on the compression flange of both the .50 and 1.5 mm (0.020 and 0.060 inch) gauge material when the lead overlay was used.⁽¹²⁾

TABLE I-12. RUBBER FORMING SHRINK FLANGE LIMITS (2000 psi)⁽³⁰⁾

Elastic Buckling Limits - (H/T)

Material	Temperature °C	Pressure Limits H/T	Critical Ratio R _D /T	$\frac{H/R}{T - H/R}$ K @ °C	For Various (H/R) Ratios mm (Inches)											
					.025 (.001)		.050 (.002)		.127 (.005)		.178 (.007)		.254 (.010)		.381 (.015)	
					R _D /T	H/T	R _D /T	H/T	R _D /T	H/T	R _D /T	H/T	R _D /T	H/T	R _D /T	H/T
2024-T3	R.T.	7.4	469	.029 R.T.	69,930	70	24,950	50	6368	32	3833	27	2277	23	1249	19
Ti-8-1-1	R.T.	9.5	2143	.008 R.T.	47,952	48	16,966	34	4378	22	2621	18				
TZM Moly	R.T.	8.8	1576	.015 R.T.	91,908	92	32,435	65	8358	42	5114	36	2970	30	1606	24

TABLE I-13. RUBBER FORMING STRETCH FLANGE LIMITS (30)

Material	Temperature °C	Pressure Limits	Critical Ratio	$\frac{H}{R}$ K	θ °C	$\frac{1}{H/R}$					
						For Various (H/R) Ratios mm (Inches)					
						.25 (.01)	.50 (.02)	1.27 (.05)	2.54 (.10)	5.08 (.20)	7.62 (.30)
		H/T	R _D /T			R _D /T	H/T	R _D /T	H/T	R _D /T	H/T
TZM MoIy	R.T.	17	144	.19	R.T.	5555	55	1989	39	567	27
TZM MoIy	260	16	150	.19	R.T.	5858	58	2142	42	588	28
Ti-8-1-1	R.T.	14	138	.13	R.T.	3535	35	1275	25	378	18
2024-T3	R.T.	18	82	.28	R.T.	4343	43	1530	30	462	22
										132	22
										95	22

Before Forming

After Forming

FIGURE I-20. ROOM TEMPERATURE HYDROFORMING MOLYBDENUM (TZM) CURVED CHANNELS
(LEAD OVERLAY)

FIGURE I-21. ROOM TEMPERATURE HYDROFORMED PARTS MOLYBDENUM (TZM)
CURVED CHANNELS

To eliminate wrinkles forming was done in a Sheridan Gray hot press. In this press a clamping pressure holds the face of the channel against the form block while a second force applies pressure against the flanges. Heat was available for application in this press, if required. Various pressures and temperatures have been used in order to reduce and/or eliminate the preformed wrinkles. It was found that final forming could be accomplished at 93°C (200°F). The wrinkles were not completely eliminated but the surface's contours are flat enough to fall within sheet metal tolerances.⁽¹²⁾

5.8 Spinning

Spinning is a very popular and satisfactory method of forming molybdenum and its alloys into symmetrical sheet metal parts. The advantages of the spinning process include low tooling cost, short set up time, and relatively close dimensional tolerances. Cross rolled sheet is preferred for spinning because it has more isotropic properties. Generally, the metal sheet to be formed is mounted on a heavy spinning lathe with one or preferably two forming rollers. Oxypropane or oxyacetylene torch(es) heat the work piece to the working temperature. Very thin sheet can be worked at room temperature, however, the usual temperature is 482°C (900°F) or greater. The spinning sequence must minimize the time at temperature to prevent excessive oxidation. The total exposure times at temperature range from 1/2 to 8 hours. Molybdenum should receive a stress relief immediately after each spinning preform step. The stress relief consists of heating the part with the torch(es) for 3 minutes at approximately 871°C (1600°F) and then allowing the part to slowly cool..

Operator skill is a very key factor in the success of the operation. The correct procedure with regard to spinning speed and application of the forming forces must be varied for different gages of sheet material. Lubrication is necessary to prevent galling of the work piece by the forming tool. Molybdenum disulfide or graphite can be used as lubricants. (3, 11, 16, 30, 31, 32, 35, 36, 64, 75, 77, 87)

The optimum forming temperature curves for spinning reported by Wood, et al,⁽³⁰⁾ are shown in Figure I-22. To prevent oxidation, the forming temperatures should be maintained as low as practical. Stratton⁽³⁾ reports forming temperatures of 593°C (1100°F) and heating the tools to $482 \pm 37^\circ\text{C}$ ($900 \pm 100^\circ\text{F}$).

The forming limits tables by Wood⁽³⁰⁾ are presented in Table I-14. Instructions for using these tables are as follows:

- ° Calculate D_D/T ratio from given dimensions.
- ° Interpolate the D_D/T ratios and corresponding D_B/D and H/D_D values to determine the required D_B/D_D and H/D_D ratios. Multiply the required D_B/D_B value by the H/D_D by D_D to determine the maximum cup depth (H).

5.9 Drawing

This process can be performed using standard practices provided the proper temperature and a slow forming rate is used. The sheet material should be cross-rolled as uniformly as possible to develop properties as isotropic as possible. The material could have a ball test or Olsen cup test called out for incoming inspection to check for isotropic properties. The two types of drawing are shown in Figure I-23. In the double action drawing process, pressure is maintained on the part from two directions. In the single action drawing process, the part is free to draw, thus the amount of clearance provided for movement of the material is critical.

The deep drawing forming limits reported by Wood, et al,⁽³⁰⁾ are shown in Table I-15. Instructions for using the forming limit table are as follows:

- ° Calculate D_D/T ratio from given dimensions.
- ° Interpolate the D_D/T ratios and corresponding D_B/D and H/D_D values to determine the required D_B/D_D and H/D_D ratios. Multiply the required D_B/D_D value by the die diameter (D_D) to determine the maximum blank diameter (D_B). Multiply the required H/D_D by D_D to determine the maximum cup depth (H).

FIGURE I-22. OPTIMUM FORMING TEMPERATURE CURVES FOR: SPINNING

TABLE I-14. SPINNING LIMIT TABLES FOR TZM (FLAT BOTTOM CYLINDRICAL CUPS)⁽³⁰⁾

A-A
Blank Diameter to Die Ratios (D_B/D_D)
and Cup Depth Ratios (H/D_D)

Temperature °C	Material Gage mm (in.)	Ratio	For Various (D_D/T) Ratios							
			25	50	100	150	200	250	300	400
R.T.	.5 (.020)	D_B/D_D	1.76	1.76	1.46	1.34	1.27	1.23	1.21	1.17
		H/D_D	.67	.67	.24	.19	.16	.14	.13	.12
R.T.	1.0 (.040)	D_B/D_D	1.76	1.76	1.46	1.34	1.27	1.21	1.16	
		H/D_D	.67	.67	.36	.26	.20	.15	.11	
R.T.	1.6 (.063)	D_B/D_D	1.76	1.76	1.44	1.27	1.18	1.14		
		H/D_D	.68	.68	.35	.20	.13	.09		
649	.5 (.020)	D_B/D_D	2.16	1.76	1.46	1.34	1.28	1.23	1.21	1.17
		H/D_D	1.18	.67	.24	.19	.16	.14	.13	.12
649	1.0 (.040)	D_B/D_D	2.16	1.76	1.46	1.34	1.28	1.23	1.21	1.17
		H/D_D	1.18	.67	.36	.26	.20	.17	.15	.12
649	1.6 (.063)	D_B/D_D	2.15	1.76	1.46	1.34	1.27	1.21	1.17	1.12
		H/D_D	1.17	.67	.36	.26	.20	.15	.12	.08

Double Action Draw Die

Single Action Draw Die

FIGURE I-23. TYPES OF DRAWING OPERATIONS

TABLE I-15. DEEP DRAWING OF TZM WITH MECHANICAL DIES (FLAT BOTTOM CYLINDRICAL CUPS)

PART SHAPE AND PARAMETERS

DIE TO BLANK DIAMETER RATIOS (D_B/D_D)

CUP DEPTH RATIOS (H/D_D)

TEMPERATURE (°C)	RATIO	FOR VARIOUS D_D/T RATIOS							
		25	50	100	150	200	250	300	400
R.T.	D_B/D_D	2.00	2.08	2.00	1.73	1.57	1.52	1.42	1.49
R.T.	H/D_D	.75	.82	.70	.48	.35	.30	.25	.19

Because of the high part temperatures involved, dies must be in contact with the part for a minimum time (to prevent cooling of the work piece). For the same reason, draw pressure is usually applied by die configuration rather than draw rings. Molybdenum disulfide and graphite have been used as lubricants. The forming temperature suggested by Stratton⁽³⁾ is 148°C (300°F) with both the tool and workpiece being heated.

5.10 Explosive Forming

Neff and Frank⁽²⁵⁾ report conducting a limited amount of study on the feasibility of explosive forming Mo-.5Zr. Conventional room temperature explosive forming methods were used. The results indicated that hot forming techniques should be used. Explosive hot forming techniques were not fully developed in the program.

6.0 JOINING

Molybdenum and its alloys can be joined by electron beam (EB) or gas-tungsten-arc (GA) welding, resistance welding, diffusion bonding, and brazing techniques. However, it appears that each of these methods has some limitations associated with the process or the final product as related to CTR component fabrication and use. These limitations will be discussed with each joining method.

6.1 Fusion Welding

Molybdenum and its alloys suffer a loss in ductility and increased ductile-brittle transition temperature (DBTT) as a result of fusion welding. Recrystallization and grain growth cannot be avoided during fusion welding, thus the resulting structure will possess brittle behavior in the vicinity of the welds at room temperature and up to as high as 150°C (302°F). This initially does not seem to be a problem since the CTR will operate at elevated temperatures, however, during a shutdown period this could cause cracking in the welds due to stressing of the structure as it cools to room temperature. Also, the possibility exists that sufficient stresses could be generated during the initial fabrication and heat up/cool down of the CTR to cause weld cracking.

Two major items effect the characteristics of the fusion weld, both relate to changes in the DBTT of the area. These are chemical changes due primarily to contamination by the atmosphere and microstructural changes due to the thermal cycle. The microstructural changes include recrystallization and grain growth, neither of which can be avoided but can be somewhat localized through choice of welding technique and procedure. Contamination by minute amounts of oxygen or nitrogen, whether in the base metal, on the faying surfaces to be welded, or in the welding atmosphere have adverse effects on the ductility of the molybdenum. Some work has indicated that for welds of reasonable ductility, the oxygen limit in the welding atmosphere is 0.005%. Nitrogen in the weld atmosphere must be reduced below 0.1% if good ductility is to be obtained⁽¹¹⁾.

The effect of carbon on the ductility of welded molybdenum is uncertain. Platte⁽³⁷⁾ indicated increased carbon content from 0.02 to 0.06 percent increased weldment ductility. Monroe, et al⁽³⁸⁾ found increased ductility

with decreasing carbon content from commercially fabricated molybdenum having 0.015 to 0.042 percent carbon. Other studies by these investigators indicated significant differences in the ductilities of weldments in lots of arc-cast molybdenum of about the same carbon content. This seemed to indicate some effect of sheet fabrication history on weldment ductility. (39)

Because of the effect on the ductility of molybdenum by contaminants such as nitrogen, oxygen and possibly carbon, it is essential that fusion welding must be conducted under extremely close controlled conditions of surface preparation and atmosphere control similar to the techniques employed for welding titanium or zirconium.

All joints in molybdenum should be designed to avoid notch effects at the joints. Weare, et al.,⁽⁴¹⁾ have shown longitudinal weld cracking to result when a notch remained at the root of a butt weld because of incomplete penetration.⁽⁴¹⁾ Longitudinal cracks also can occur with complete penetration if a notch is left at the start or end of a weld.

The steps necessary to produce acceptable welds in molybdenum with minimized chances for embrittlement problems are:

- ° Provide extreme cleanliness of the faying surfaces and adjacent areas. This involves removing the invisible as well as the visible oxide film. Electrolytic polishing seems to be a reliable method, although chemical baths are satisfactory and are usually more convenient.

- ° Control the welding atmosphere carefully with respect to oxygen and nitrogen. High purity (99.995+ %) argon and helium are a necessity. If purity is questionable, the gases should be purified before use.

- ° Careful preparation of parallel edges and proper jigging are desirable to avoid cracking. The clamping loads should be compressive, and the fixtures should be released as soon as welding is completed to permit the weldment to cool unstressed.

- ° A preheat at 204°C (400°F) and a postheat at 871/982°C (1600/1800°F) in hydrogen or vacuum have been found to give favorable results and are decidedly beneficial when welding complex assemblies.

- ° Minimize the width of the weldment and the heat affected zone.

- ° Prevent stress risers in weld and heat affected zone.

Corner or edge welds are generally easier to make than butt welds; while butt welds in turn are usually simpler to produce than fillet welds. With sheet, butt welds are normally employed on thicknesses up to 2.38 mm (3/32 in.); greater thicknesses require multiple passes in a V-butt joint. Filler wire additions are needed for all multiple-pass weldments, and a 204°C (400°F) preheat should be maintained during welding. If multiple passes are used on long weldments, the weld metal may be oxidized when it comes out of the protective atmosphere. In such cases, chemical cleaning or electrolytic polishing is necessary before the next pass. Filler wire lessens the need for highly accurate fitting of details and reinforces the weld. Because of its lower gas content; arc-cast molybdenum is preferred for filler wire when ductile welds are desired. Some filler-wire alloys, such as the 50% Mo-50% Re composition, have better ductility than unalloyed molybdenum or lower-alloy molybdenum grades.

Amperage and travel speed depend largely on the fixtures and chills used, and therefore must be established by trial. It has been determined that the weld ductility increases with the travel speed, provided there is sufficient time for complete penetration and the shielding is adequate to prevent contamination by atmospheric gases.

A stress relief of the welded joint is recommended in all cases; the temperature and time selected should not permit recrystallization of the parent metal unless considerable forming is to be done. The room-temperature ductility of the weld and heat-affected zone will usually be improved markedly by roller leveling or roll planishing at about 315°C (600°F), or by

grinding after welding to produce a smooth surface and to remove any possible microcracks that might serve as stress raisers.

For gas-tungsten-arc welding of molybdenum and its alloys, a non-consumable tungsten electrode is generally preferred for thicknesses up to 6.35 mm (1/4 inch); filler-wire additions are used for thicknesses over 2.38 mm (3/32 inch). Consumable electrodes may come into consideration for heavier sections. Manual arc welding is feasible but not as reliable as automatic machine welding. Either helium or argon, or mixtures of these two - sometimes with hydrogen - are used; the choice depends on the precise welding setup. Helium is selected by some because of the greater heat produced at the arc. An inert-gas box is not needed if shielding is adequate; suitable shielding usually involves both trailing and leading shields as well as backup gas.

The electron beam welding of unalloyed molybdenum and molybdenum alloys in general produce welds with less porosity and cracking. The heat affected zone and weld bead are narrower, which is a characteristic trait of EB welding, and the grain size in the weld bead are smaller.^(11, 12, 13, 14, 16, 26, 27, 32, 34, 42, 43)

Corrugated panels for the control surface shown in Figure I-4 were EB welded and performed satisfactorily during component testing.

Rigorous processing steps were used by Sinclair⁽¹⁴⁾ to weld molybdenum-.5 Ti for the preparation of samples for bend transition temperature tests. The procedure is included below.

Specimens were cut from the sheet material with a water-cooled abrasive cutoff wheel. The lengths of the specimens were parallel to the final rolling direction of the sheets. All specimens were 5.08 mm (2 inches) in length. Edges of all bend specimens were hand lapped with 280-grit silicon-carbide paper and inspected for laminations under a binocular microscope at a magnification of approximately 15. The welding fixture is shown in Figure I-24.

FIGURE I-24 END VIEW OF WELDING FIXTURE, LENGTH 22.86 CM (9 IN.)

Prior to welding, all specimens were vapor degreased and chemically cleaned. A cleaning method was selected that consisted of the following steps:

- ° Five-to-10 minute dip in hot 65 to 82°C (150 to 180°F) deoxidizer consisting of 10 percent sodium hydroxide, 5 percent potassium permanganate, and 85 percent water (by weight).
- ° Cold-water rinse.
- ° Approximately 5-minute dip in 15 percent sulfuric acid, 15 percent hydrochloric acid, 70 percent water (by volume) with 6 to 10 grams of chromic acid added per 100 cc.
- ° Hot-water rinse.
- ° Air drying.

During cleaning, specimens were held in a basket fabricated from perforated molybdenum sheet. Thereafter, until welding was completed, specimens were handled only with tweezers.

The chamber was pumped down to a pressure of 1.33×10^{-2} Pa (10^{-4} torr) or less, and then back filled with helium to approximately 2/3 atmosphere (as indicated by a Bourdon gage), in order to support a stable arc. Specimens were preheated to approximately 148°C (300°F) prior to welding by infrared lamps within the welding chamber.

Gettering was employed to improve the atmospheric purity in the weld box before the molybdenum strips were welded. Either bead-on-plate runs were

made on titanium sheet prior to welding or titanium filaments located near weld specimens were heated to incandescence prior to and during welding.

A welding speed of 17.78 cm (7 inches) per minute was used for welding all of the bend-test specimens. A motor-operated screw moved the welding fixture and specimens past the stationary welding head at constant speed. A 1.58 mm (1/16-inch) diameter, 2-percent-thoriated-tungsten electrode was selected for welding both the .5 and 1 mm (0.020- and the 0.040-inch) sheet material. Fusion of the sheet material was accomplished by use of direct-current straight-polarity arc welding; no filler metal was added. Power input to the arc for welding the 1 mm (0.040-inch) molybdenum at 17.78 cm (7 inches) per minute varied from 120 to 180 amperes at 15.5 volts. The 1 mm (0.040-inch) molybdenum 0.5-percent-titanium sheet required from 110 to 190 amperes at 15.5 volts. The welding fixture temperature went up as the welding progressed, and gradual reduction of the welding current to avoid burn-through was necessary as welding progressed. These reductions were based on visual estimation of the width of the fused zone. The .5 mm (0.020-inch) molybdenum 0.5-percent-titanium sheet required 80 to 85 amperes at 15.5 volts for welding. Since these specimens warped too badly during welding to permit bend testing, .5 mm (0.020-inch) molybdenum was not welded.

The results of Sinclair work are presented in Figure I-25. The transition temperature was arbitrarily defined as the temperature at which the bend angle of fracture was 90°.

Moorehead, Slaughter and DiStefano^(44, 45) welded joints typical of those that could be expected in a reactor design, such as tube-to-header, cylindrical girth, and tube-to-tube butt joints during development and construction of a molybdenum test stand.

The tube-to header joint used is shown in Figure I-26. A critical feature of this joint is the tight fit required between the hole and the tube. A Class LC5 (Machinery's Handbook, 19th Ed, Industrial Press, New York, 1972, p.1523) was recommended. The electron beam welding machine used was the high voltage, low current type (150 KV, 0.040 A max.). The weld parameters are shown in Table I-16. The conventional method of rotating the

FIGURE I-25. TRANSITION TEMPERATURES AFTER VARIOUS TREATMENTS

FIGURE I-26. TUBE-TO-HEADER JOINT

TABLE I-16. PARAMETERS FOR ELECTRON BEAM WELDING TWO SIZES OF MOLYBDENUM TUBING TO A BACK-EXTRUDED HALF SECTION

	Tube-to-Header Joints	
	9.52 mm (0.375 in.) OD	28.58 mm (1.125 in.) OD
Joint Type	Corner Flange	Corner Flange
Joint Thickness, mm (in.)	1.27 (0.050)	3.05 (0.120)
Accelerating potential, kV	120	120
Beam Current, mA:		
Preheat	-	11
Weld	5	23
Number of Revolutions		
Preheat	-	6
Weld	1-1/2	1-1/4
Travel Speed, mm/sec (ipm)	5.9 (14)	5.9 (14)
Focus, A defocus	0.015	0.015
Work Distance, cm (in.)	15.2 (6)	30.5 (12)

work under the beam provided more reproducible results than rotating the beam around the part.

Cylindrical girth joint design is shown in Figure I-27. Both GTA and EB welding was used for this joint. The GTA welds were made in a vacuum purged argon backfilled glove box. The chamber was evacuated to 6.7×10^{-3} Pa (5×10^{-5} torr) or less and back-filled with argon having minimum purity of 99.997%.

Filler metal was 1.5 mm (0.060 inch) diameter low carbon, low oxygen welding rod prepared commercially from cast stock. The vessel was tacked in three locations and then manually rotated during welding. The electrode was 2% thoriated tungsten, 3.18 mm (0.125 inch) diameter. No auxiliary preheating was required for the GTA welds because the high conductivity of molybdenum leads to a rapid distribution of heat through the parts (i.e., preheat) before the fusion temperature is reached at the joint.

Electron beam girth welds were made with a rotary fixture. A general requirement for welding with this process, if filler metal is not added, is that the joint must be held tightly together so that coalescence will occur and so that the resulting weld bead will not be underfilled. The harmful effects of an underfilled, concave weld bead are especially pronounced in crack sensitive materials such as molybdenum.

Unfortunately, the complex geometry of the vessel half-sections with their protruding tubes and internal baffle plates made the application of end loading by conventional means quite difficult. To overcome this problem, a technique was developed in which three .81 mm (0.032 inch) diameter molybdenum pins through the step joint were used to hold the halves in intimate contact during welding. These pins were subsequently fused into the weld.

The parameters for electron beam welding the cylindrical girth joint are given in Table I-17. Note that extensive preheating was carried out with the defocused beam before welding to minimize the possibility of cracking.

FIGURE I-27. GIRTH JOINT DESIGN

TABLE I-17. ELECTRON BEAM WELDING PARAMETERS FOR CYLINDRICAL GIRTH JOINT (44, 45)

Joint Type	Step
Joint Thickness, mm (in)	2.39 (0.094)
Accelerating potential, kV	150
Beam Current, mA:	
Preheat	12
Weld	25
Number of Revolutions	
Preheat	6
Weld	1 1/4
Travel Speed, mm/sec (ipm)	14 (32)
Focus, A defocus	0.015
Work Distance, cm (in.)	10 (4)

Tube-tube butt welds, in five different sizes of molybdenum tubing were successfully made in an argon filled glove box by the gas tungsten-arc process, both manually and with an automatic orbiting-arc technique. Using either technique welds were produced that were helium leak-tight and had little or no porosity as shown by radiographic and metallographic examination.

The orbiting arc process was used both inside a glove box and outside the argon chamber. Rubber sleeves were adapted to the welder head to provide atmosphere coverage. The results were not as reproducible outside the glove box.

Weld inserts, such as the one shown in Figure I-28 between two tees, were used to control root reinforcement and joint misalignment when orbiting-arc welds were made in these tubing sizes. Because it protrudes slightly above the tube surface, it also provides a small amount of filler metal for the joint, thus producing convex weld beads, which were found to be less prone to cracking than concave beads.

The procedure for butt welding of 6.35 mm OD x .5 mm wall (0.250 inch OD x 0.020 inch wall) molybdenum tubing is given in Table I-18. The important features of the welding cycle are the relatively long portion at a lower "initial current", which preheats the joint without fusion and the gradual increase in rotational speed to minimize "weld bead widening", which occurs in tube welds as the overlap portion is approached.

All of the above weld details for the work of Moorehead, Slaughter and DiStefano had the following pretreatments prior to welding:

1. Degrease with acetone.
2. Immerse for 5 minutes in a 65 - 80°C (150 - 175°F) solution of 10 wt % sodium hydroxide, 5 wt % potassium permanganate, and 85 wt % distilled water.
3. Rinse in flowing tap water, brushing to remove smut.
4. Immerse for 5 - 10 minutes in a room-temperature solution of 15 vol % sulfuric acid (95 - 97% H₂SO₄), 15 vol % hydrochloric acid (37 - 38% HCl), 70 vol % distilled water plus 6 - 10% chromium trioxide (CrO₃).

FIGURE I-28. DESIGN OF INSERT FOR TUBE-TO-TUBE WELDS

TABLE I-18. PARAMETERS FOR WELDING BUTT JOINT BETWEEN 6.35 mm OD X 0.5 mm Wall
(1/4 IN. OD X 0.020 IN. WALL) MOLYBDENUM TUBING USING AN ORBITING-
ARC WELD HEAD INSIDE AN ARGON FILLED GLOVE BOX

JOINT TYPE - SQUARE BUTT WITH INSERT

JOINT THICKNESS - 0.64 mm (0.020 IN.)

ELECTRODE:

EW-Th2 - 1.57 mm (0.062 IN.) DIAM.

30 DEG CONICAL TIP

ARC LENGTH - 0.81 mm (0.032 IN.)

GAS FLOW THROUGH HEAD - .14 m³/h (5 cfh) Ar

WELDING CONDITIONS:

INITIAL:

CURRENT - 30A

TIME - 6 sec

WELD:

CURRENT - 56A

TIME - 10 sec

FINISH:

CURRENT - 1A

TIME - 5 sec

TRAVEL SPEED:

INITIAL - 3.3 mm/sec (7.8 ipm)

WELD - 4 mm/sec (9.4 ipm)

FINISH - 4 mm/sec (9.4 ipm)

5. Rinse with tap water.
6. Rinse with distilled water.
7. Dry with hot air.

Although in this study the investigators did not find any correlation (as far as leak-tight welds were concerned) with the length of time between cleaning and welding, in some cases where parts had been excessively handled after the initial cleaning, they did take the precaution of repeating steps 1 and 4-7 of the procedure immediately before welding.

After chemical cleaning, all components were given a vacuum stress relief treatment for 60 min. at 870-900°C (1600-1650°F) at a pressure of 6.7×10^{-4} Pa (5×10^{-6} torr) or less. The combination of the chemical and thermal treatments left the components with surfaces that were a lighter gray than those in the as-received condition with no noticeable grain boundary attack.^(44,45)

Krakowski, et al.⁽⁴⁶⁾ found that the difficulties anticipated in achieving good molybdenum and TZM welds are not severe enough to warrant exclusion of it as a candidate structural material in the CTR. The precautions that they suggest are included here as a summary to the welding section:

- ° Arc-melted material should be used exclusively. Pressed and sintered molybdenum is too porous and impure to render strong, defect-free welds.
- ° Extreme care should be exercised in maintaining a pure and inert environment during the welding.
- ° Proper pretreatment and post-treatment (stress relief, joint design, pre-heating) procedures should be adopted.

6.2 Brazing

This joining method has to be given serious consideration for use in CTR fabrication. Molybdenum has been brazed in the electronics industry for years, however these joints do not require high strengths. The CTR requirements are for structural joints with sufficient strengths at elevated

temperatures approaching 1100°C. Before brazing could be used for CTR fabrication, several requirements must be considered. Among these are the strength of the joint required at elevated service temperature, the resistance of the braze alloy to corrosion or erosion by liquid metals and the effect of irradiation on the braze joint. A possible problem may arise because the proposed brazing temperatures are approaching the recrystallization temperature of molybdenum and its alloys. This, assuming that a recrystallized structure is undesirable, almost necessitates using a relatively low melting point braze alloy, less than about 1300°C (2372°F) to minimize the recrystallization. Even though there are alloys in this range and some can be given diffusion cycles that develop remelt temperatures higher than the brazing temperature, the strengths of the resulting joints may not be sufficiently high.

Satisfactory brazed joints have been made using all common brazing processes. Furnace brazing has the advantage of being adaptable to large and complex parts. Disadvantages are limited temperature range and relatively low heating rates, which may result in the recrystallization of molybdenum. Torch brazing could be used provided adequate fluxes for high temperature could be produced. Fair protection has been offered at temperatures to 1400°C by a flux containing 50 percent "Eutector 189" and 50 percent CaF_2 mixed with alcohol and used in conjunction with a precoating of "Handy Flux".⁽⁴²⁾

Induction and resistance brazing have also been used successfully.

All of the discussion in the welding section pertaining to impurities, atmospheres, recrystallization, etc. apply to brazing.^{(13, 16, 40, 42).}

There is a lack of brazing property data and that which does exist is for short term tests. Long term elevated temperature properties including tensile, yield and creep are not available and will be required before brazed joints in molybdenum can be considered for CTR use.

A list of some brazing alloys that have been used on molybdenum is

presented in Table I-19. Tensile tests of some brazed butt joints⁽⁴²⁾ are shown in Table I-20.

The Ti-25Cr-3Be alloy, which exhibited a liquidus temperature of 1110°C (2030°F), was most promising for brazing TZM honeycomb structures. Maximum processing temperature required for this alloy was 1260°C (2300°F). Ductile closed-cell honeycomb panels were produced which exhibited remelt temperatures of 1704°C (3100°F) and service capabilities at 1593°C (2900°F). Applicability of the Ti-25Cr-3Be braze alloy and associated processing parameters was demonstrated on complex edge-attachment joints.^(47, 49) This technique may allow short time use at these temperatures, but extended time data for CTR use is not available.

The Ti-8 Si alloy is brazed at 1398°C (2550°F), giving a service temperature (not clearly defined what service temperature really means) of 1648°C (3000°F). However, it causes at least partial recrystallization and extreme brittleness with an elongation of 0 percent.⁽²⁶⁾

High remelt temperature brazing was based on diffusion sink and, to some extent, reactive brazing concepts. Diffusion sink brazing relies upon the reaction of a braze alloy with the base material during the brazing cycle and during a post-braze diffusion treatment. Braze alloy-base material interdiffusion results in a new solid solution alloy in the joint with a high melting temperature. Reactive brazing involves use of a braze alloy containing a strong melting temperature depressant selected to react with the base material to form discrete high melting intermetallic compound particles during brazing and diffusion treatment. By removing the depressant in this manner, joint remelt temperatures were increased. Larger increases were attained by permitting additional base alloy diffusion into the braze joint matrix.⁽⁴⁷⁾

Exothermic brazing as discussed by Long⁽⁵⁰⁾ utilizes the heat from an exothermic reaction to melt the braze alloys. This may offer some advantages for CTR fabrication at the site and for repair.

REFRACTORY METALS
FABRICATION

FINAL REPORT

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TABLE I-19. HIGH-TEMPERATURE BRAZING ALLOYS FOR MOLYBDENUM

Alloy Name	Composition, per cent	Liquidus, °C °F	
<u>Pure Metals</u>			
Copper	100 Cu	1082	1980
Nickel	100 Ni	1454	2650
Palladium	100 Pd	1571	2860
Platinum	100 Pt	1774	3225
<u>Nickel Base</u>			
Wall Colmonoy No. 6	78Ni-18Cr-4B	1066	1950
Nickel-Titanium	84Ni-16Ti	1288	2350
Hastelloy C	57Ni-17Mo-16Cr-6Fe-4W	1304	2380
Monel	67Ni-30Cu	1349	2460
Inconel	80Ni-14Cr-6Fe	1393	2540
<u>Iron Base</u>			
18-8 Stainless Steel	18Cr-8Ni-Bal.Fe	1427	2600
25-20 Stainless Steel	25Cr-20Ni-Bal.Fe	1454	2650
<u>Cobalt Base</u>			
Haynes Alloy 21	54Co-27Cr-6Mo-3Ni	1399	2550
Haynes Alloy 25	55Co-20Cr-15W-10 Ni	1427	2600
<u>Niobium Base</u>			
Niobium Nickel	52Nb-48Ni	1191	2175
<u>Palladium Base</u>			
Palladium-Aluminum	93Pd-7Al	1177	2150
Palladium-Nickel	53Pd-47Ni	1204	2200
Palladium-Nickel	60Pd-40Ni	1260	2300
Palladium Copper	60Pd-40Cu	1204	2200
Palladium Copper	65Pd-35Cu	1260	2300
Palladium Copper	70Pd-30Cu	1316	2400
Palladium-Silver	50Pd-50Ag	1316	2400
Palladium-Silver	60Pd-40Ag	1371	2500
Palladium-Iron	70Pd-30Fe	1316	2400
Palladium-Iron	50Pd-50Fe	1316	2400
<u>Molybdenum Base</u>			
Molybdenum-Boride	Mo-B Eutectic	1899	3450
Molybdenum-Reuthenium	Mo-Ru	1899	3450
<u>Titanium Base</u>			
Titanium-Chrome-Beryllium	Ti-25Cr-3Be	1110	2030
Titanium-Silicon	Ti-8Si	1399	2550
Titanium-Vanadium	Ti-30V	Service Temp.	1371 2500
Titnaium-V-Cr-Al	Ti-3Al-11Cr-13V	Service Temp.	927 1700
Titanium-Zirconium		Service Temp.	1232 2250
<u>Vanadium Base</u>			
Vanadium-Niobium	V-35Nb	Service Temp.	1204 2200

TABLE I-20. TENSILE STRENGTHS OF BRAZED BUTT JOINTS IN MOLYBDENUM

Brazing Alloy	Test Temperature		Tensile Strength	
	°C	°F	MPa	psi
70Pd-30Cu	816	1500	173-239	25,200-34,800
	982	1800	66.8-95.8	9,700-13,900
	1093	2000	47.5	6,900
84Ni-16Ti	Room	Room	180.5-191.5	26,200-27,800
	Room	Room (a)	152.9-195.7	22,200-28,400
	982	1800	121.3-124.7	17,600-18,100
	982	1800 (a)	119.2-126.1	17,300-18,300
52Nb-48Ni	Room	Room	149.5	21,700
	Room	Room (a)	175.7-273.5	25,500-39,700
	982	1800	130.2	18,900
	982	1800 (a)	119.2-137.1	17,300-19,900
50Pd-50Fe	Room	Room	340.4	49,400
	Room	Room (a)	299.7	43,500
	982	1800	119.2	17,300
	982	1800 (a)	45.5-49.3	6,600-7,150

(a) Heated for 24 hours at 982°C (1800°F) in vacuum prior to testing.

The exothermic heating concept requires the same metallurgical considerations as for conventional brazing techniques; however, the exothermic heating concept offers advantages which make it more flexible than existing techniques. These advantages are as follows:

- ° The short times at or near brazing temperature allow temperatures on the order of 1760°C (3200°F) to be used with a minimum of base metal recrystallization and braze alloy-base metal interdiffusion.

- ° The short times at temperature and the inherent reducing natures of the exothermic reaction tend to minimize refractory metal oxidation, thus reducing or possibly even eliminating the need for protective atmospheres.

To develop a successful brazing process for refractory alloys wherein the heat for brazing is supplied by an external reaction, it is necessary to select an exothermic mixture which, when reacted,

- ° Would not attack the base metal either by a chemical action or by producing metallic or ceramic phases, which adhere to the base metal surfaces and are difficult to remove.

- ° Would produce the necessary heat for brazing without the use of excessive amounts of reactants.

- ° Would preferably act as a "getter" during the reaction to reduce base metal oxidation, either by dissolving the oxide film formed or by protecting the surface from oxygen penetration from the atmosphere.

- ° Would not produce reaction products which prevent maximum heat transfer to the braze bondline and rapid cooling from the brazing temperature.

The criteria for selection of the braze filler metal are the same as for any standard brazing process in that (1) it must be compatible with the base metal (i.e., it must not form eutectics or brittle intermetallics),

and (2) it must possess the necessary mechanical, physical, and corrosion-resistant properties for the intended use at the projected service temperature, and (3) preferably should be commercially available in foil form.

An investigation was conducted to determine the effect of exothermic heating on the brittle-ductile transition temperature of molybdenum, tungsten, and TZM alloy (Table I-21). Unalloyed molybdenum metal, as received from the supplier, had an extremely low transition temperature, (approximately -143°C (-225°F) which increased to approximately 10°C (50°F) after exothermically heating and accounted for the ductility still evident in the molybdenum after exothermic heat exposure even though recrystallized. TZM alloy, .304 mm (.012 in) thick, also showed an increase in transition temperature to about 65°C (150°F), which was greater than could be anticipated, based on the examination of the metallographic structure which showed about 50% recrystallization.

An alloy with a slightly higher short-time recrystallization temperature may not recrystallize at all as was evident for the TZM alloy brazed at 1704°C (3100°F) with Premabraz 205, which showed only 50% recrystallization in the center of the overlap, 10% at the edge of the faying surfaces, and no recrystallization beyond the faying surfaces. This type of brazing gives a highly localized heat.

The results of the tensile tests on as-received and exothermically-heated niobium and tantalum indicate that there was some oxygen and/or nitrogen pickup during the brazing cycle. This is indicated both by the fact that the heated tensile specimens broke adjacent to the area in contact with the exotherm and by the reduction in elongation of the heated section, thus showing a strengthening effect in the heated section due, no doubt, to gas contamination. However, this contamination seems to be minimal and far less than one would expect for an air-brazing process.

6.3 Diffusion or Solid State Bonding

This joining technique appears to be very attractive for CTR use,

TABLE I-21. EFFECT OF EXOTHERMIC HEATING ON DUCTILE-BRITTLE TRANSITION TEMPERATURE
Brittle-Ductile Transition Temperature

REFRACTORY METAL	As-Received				After Exotherm Heat Exposure			
	Brittle °C	°F	Ductile* °C	°F	Brittle °C	°F	Ductile* °C	°F
Molybdenum .75 mm (.030 in) thick	-157	-250	-143	-225	-4	25	10	50
TZM Alloy .304 mm (.012 in) thick	-79	-110	-71	-95	52	125	66	150
Tungsten .75 mm (.030 in) thick	218	425	232	450	288	550	300	575

* Bend Angle with 3T Radius Radius 24°C (75°F)

** Constant Ram Rate 25.4 cm (10 Inches) per Minute

however, there has been only limited investigation conducted. If a suitable process for diffusion bonding could be developed as to not recrystallize the molybdenum, the ductility problems associated with a recrystallized welded structure would be alleviated.

There are three types of diffusion bonding: yield stress controlled (pressure welding, roll bonding); diffusion controlled bonding; and creep controlled bonding. In yield stress controlled bonding the pressures are above the yield stress and diffusion times are very short. In diffusion controlled bonding the pressures are high, but below the yield stress. Bond cycles may be from 3 minutes to 3 hours. In creep controlled bonding low pressures and high temperature, below the recrystallization temperature, for long times (up to 24 hours) are used.⁽⁵¹⁾

The use of intermediate materials in the faying surface to be bonded can reduce the required pressure and time for bonding. This occurs because the intermediate foils deform under less pressure than the molybdenum to give intimate contact and also can act as diffusion aids. The major disadvantage of soft intermediate metals is that the joint strength can decrease rapidly with increasing temperature, so that failure occurs in the intermediate material. By reducing the intermediate thickness to a few microinches, this effect can be minimized.^(42, 51)

The key factors affecting the success of diffusion bonded joints are intimate contact of clean oxide free surfaces so that diffusion can occur across the bond line.

Dunning and Metcalfe⁽⁵²⁾ have conducted diffusion bonding studies on TZM using several intermediate foils. They used titanium, niobium, vanadium, and molybdenum foil interleaves. The most favorable results were obtained with the titanium intermediates. Bonding was conducted at pressures of 68.9 MPa(10 ksi) and temperatures of 1010 and 1426°C (1850 and 2600°F). The general conclusion reached by Dunning & Metcalfe is that stable, high strength joints can be attained in nearly all systems. Three main requirements may be cited for the intermediate foil. These are: adequate strength

at temperature; substitutional diffusional stability; and no "sink" action for interstitials. Although systems such as Cb-752-titanium and TZM-titanium have been selected for use in diffusion bonded structures, prior work and the current study show that these are not optimum choices. To the disadvantage of the low strength of pure titanium must be added the interstitial sink effect. The latter is very critical with alloys such as TZM where the removal of carbon to an interstitial sink leads to secondary effects including weakening of the TZM, reduction of recrystallization temperature, and increase of the ductile-brittle transition temperature following recrystallization and grain growth.

The selection of suitable intermediate foils for carbon-containing alloys such as TZM presents acute problems. None of the typical intermediate metals are suitable: titanium, zirconium, hafnium, vanadium, niobium, and tantalum can act as interstitial sinks. Molybdenum foil appears to be compatible and may be the only choice if alloy stability is critical. Butt joints appear to be more susceptible to this effect than lap joints, suggesting that carbon diffusion is primarily along grain boundaries. Working sheet or bar elongates the grains so that longitudinal diffusion will be faster than in a transverse direction. This effect is probably related to the higher concentration of titanium and zirconium in the grain boundaries of the TZM rather than to a grain boundary effect in molybdenum.

Johnson, Udin, and Wulff⁽⁵³⁾ carried out upset forge welding of molybdenum in hydrogen, chlorine, helium, carbon tetrachloride or water. Best results were obtained with carbon tetrachloride or water. Lithium or sodium in the joint offered some improvement when welding under carbon tetrachloride. Some welds were produced that had ductilities approaching that of the parent metal. The success of the process was based on control of three factors:

- ° Peak temperatures had to be carefully regulated to allow forging of the recrystallized zone, but without excess fusion at the interface.
- ° Time at temperature had to be minimized.
- ° Fast extensive upset was required.

6.4 Resistance Welding

Resistance seam welding could possibly be used for CTR fabrication if joint strengths are sufficient and if no problem results because of the recrystallized nugget or lack of vacuum tightness.

The resistance welding of small molybdenum parts has been commercial in the lamp and electronic industries for many years. The electronic industry also frequently sandwiches nickel or platinum foil between the molybdenum sheets or wires to give a combination braze-weld. Recent developments have shown that spot welds with excellent structural properties can be produced in thin sheet and strip; this type of welding is especially good for making molybdenum skin or all-molybdenum sandwich structures.

Either AC or DC welding equipment can be used. A condenser-discharge type of welder, or an ignitron type with 1/2-cycle timer has been satisfactory. Welding conditions should be such as to minimize contamination by air. This may be done by welding under chlorinated solvents or by suitable adjustment of times and currents to decrease the period when the hot metal is exposed to air. By proper use of postheat and forging cycles, it is possible to warm work the weld and thus to obtain spot welds with ductility and strength characteristics approaching the optimum values for molybdenum.

One problem with spot or seam welding is sticking and deformation of the electrodes. Copper, copper-alloy, molybdenum and tungsten electrodes have been tried but none has proved completely satisfactory. Cooling or refrigeration of the electrodes may be helpful.

If the design permits, one of the sheets to be joined by protection welding should be dimpled or sandblasted. In the case of spot welds, it has been found desirable to etch the surfaces of both sheets to be joined. One method involves immersion for about ten seconds at 90°C (195°F) in a solution containing 18,900 cc (five gallons) of concentrated sulfuric acid, 375

grams of chromic acid, 950 cc (one quart) of hydrofluoric acid, and 95 cc (0.1 quart) of concentrated nitric acid; the sheets should then be immersed in a hot chromic-acid glass-cleaning solution until the blue oxide disappears⁽¹¹⁾.

Peck⁽⁵⁴⁾ conducted an investigation to determine the causes of electrode sticking. His conclusions and recommendations are as follows:

° Two mechanisms contributing to electrode sticking appear to be: (a) mechanical bonding, (b) brazing when using copper electrodes, and (c) diffusion or solid state bonding. The first mechanism predominates when no melting occurs at the electrode sheet interface. A braze joint forms when welding with copper electrodes at sufficiently high current to cause melting at the electrode-sheet interface. Diffusion bonds are also formed when the electrode-sheet interface temperature is sufficient to cause recrystallization of the electrode.

° Welding parameters, particularly current, have a pronounced effect on sticking. The sticking tendencies can be reduced but not eliminated by welding at a low electrode force and as low a welding current as possible and still produce a sound nugget of acceptable soundness. Weld time, i.e., time of current flow should be kept to a minimum. The same can be said of welding impulses. Single impulses of 5 cycles or less were found to produce less sticking than multiple impulses and large current flow times.

° The thermal and electrical conductivity of the electrode was found to significantly influence electrode sticking. RWMA Class 1 copper electrodes were generally less sensitive to sticking than the higher alloyed electrodes and copper impregnated type electrodes. This is attributed to the higher thermal and electrical conductivities of the Class 1 electrode.

° Variation in sheet and electrode surface finish had little influence on electrode sticking tendencies. This may be due to the severity of the sticking which overshadowed any benefit derived by roughening faying surfaces. In keeping with acceptable welding practice, the

surface of the electrode should be maintained at a smooth machined finish while the faying surfaces may be roughened. The outer sheet surfaces need not be prepared. There were indications that the presence of the as-received oxide on Cb-752 reduced electrode sticking tendencies. This effect was not significant when welding Ta-10W or TZM alloys.

° Variations in electrode contour had no observable influence on electrode sticking.

° Cryogenic cooling of the welding electrodes by using liquid nitrogen as the coolant offers a means of eliminating sticking when producing cast nuggets in refractory alloys. This technique which has been developed and put into use by Ling-Temco-Vought Corporation⁽¹⁹⁾ also reportedly provides an improvement in mechanical properties by virtue of finer grain sizes achieved through the use of the low temperature coolant.

° Electrode sticking can be eliminated by avoiding melting at the sheet faying surfaces and thus producing solid state or diffusion bond. It is, however, not sufficient just to avoid nugget formation. The solid state bonding must be done under condition of weld current that do not overheat the electrode-sheet interface and thus produce a solid state bond between the work and electrodes. Such a bond at the electrode-work interface can lead to sticking and excessive electrode deterioration.

° Projection welding is a third method of producing strong welds in refractory metal without electrode sticking or electrode deterioration. Such welds exhibited structure consisting of a cast nugget around the periphery of the projection and a solid state bond within the annular nugget. Projections made with existing tooling were not optimum in that they collapsed before enough heating occurred to generate a weld nugget. However, the strengths obtained with the mixed weld structure were good; i.e., it may not be necessary to produce a fused projection weld to attain desired strength levels. The merit of using solid state projection welds are the same as conventional resistance solid state welding in regard to electrode sticking.

7.0 CLEANING

Cleaning is an extremely important process during fabrication of molybdenum because of the difficulties that may be encountered when forming or welding contaminated material.

Ordinary cleaning or degreasing can be done by conventional methods. Pickling is seldom a problem as metallic molybdenum is normally free scaling.

A vapor blast is the easiest way to remove a heavy oxide coating; a grit blast may also be used. When molybdenum parts for electronic tubes are grit blasted for a greater radiation surface, steel grit is recommended as other abrasives become embedded in the molybdenum and cannot be easily removed. After blasting, the parts are thoroughly cleaned in hot hydrochloric acid to remove the steel particles. (11, 42)

One of the most widely used chemical means of removing heavy oxide coatings is a molten-caustic bath, although this involves the safety hazards inherent in any operation of this type. Good results have been obtained with a bath consisting of 90% potassium hydroxide and 10% sodium nitride, operated at 315°C (600°F). Conventional molten sodium-hydroxide or sodium-hydride baths may also be used. A thin oxide film can be removed in a hot 10% solution of caustic soda in water.

The first bath requires close control because the molten salt attacks the molybdenum. No gross attack was noted when using the second bath. Salt bath cleaning should be followed by another treatment to remove light oxide films before joining. (46, 75) This thorough cleaning may be done chemically, electrolytically or by hydrogen firing.

Electrolytic polishing can be used to clean the surfaces. The following bath can be used at room temperature with the molybdenum as the anode. (11)

<u>Solution</u>	<u>Current</u>	<u>Comments</u>
1900 cc (4 Pts.) phosphoric acid 475 cc (1 Pt.) sulfuric acid 1900 cc (4 Pts.) water	1.5 to 2.1 amp/cm ² (10 to 14 amp/in ²)(30 seconds)	Dip in denatured alcohol prior to water rinsing.

Chemical cleaning provides clean surfaces free from contamination and possible embedded inclusions. Five of the numerous solutions used are listed below. The first has been found satisfactory as preparation for electroplating; the second and fourth produce the ultraclean surfaces needed for electronic applications; and the third and fifth have been developed as prior treatments for welding.

alkaline ferricyanide	aqueous solution with 300 gm/1000 cc potassium ferricyanide, 100 gm/1000 cc potassium hydroxide, one-minute dip at 26°C (80°F).
"Bell Laboratory"	aqueous solution with 80% hydrogen peroxide, 10% formic acid, five-to-ten-minute dip at room temperature.
complex acid	95 vol % sulfuric acid, 4.5 vol % nitric acid, 0.5% vol % hydrofluoric acid, 18.8 gm/1000 cc: chromic acid, 30-sec dip at 60°C (140°F).
glass cleaning	concentrated sulfuric-acid solution with 3.5 vol % saturated sodium dichromate, brief dip at 90°C (195°F).
"Ryan"	aqueous solution with 10% sodium hydroxide, 5% potassium permanganate, five-to-ten-minute dip at about 71°C (160°F), follow by pressure-spray rinse and five-to-ten-minute dip at room temperature in aqueous solution with 15% sulfuric acid, 15% hydrochloric acid and 6 to 10% chromic acid.

Similar results have been obtained with an anodic or cathodic treatment in a 70 vol % sulfuric-acid solution at room temperature. The cathodic treatment is generally followed by hydrogen firing.

Hydrogen firing will reduce molybdic-oxide films but will not remove organic solvents and embedded inclusions. It has the advantage of relieving cold strains and setting dimensions. Pure dry hydrogen is preferred, although dissociated ammonia (with no free ammonia present) may be used

if no further forming is to be done. The parts are heated to about 815/982°C (1500/1800°F) for 10/30 minutes, then cooled in the same atmosphere.

Several cleaning procedures using the above solutions are as follows:

Prior to welding all Mo-0.5Ti specimens were vapor degreased and chemically cleaned. A cleaning method was selected that consisted of the following steps:⁽¹⁴⁾

- ° Five-to-10-minute dip in hot 65 to 82°C (150 to 180°F) deoxidizer consisting of 10 percent sodium hydroxide, 5 percent potassium permanganate, and 85 percent water (by weight)
- ° Cold-water rinse.
- ° Approximately 5-minute dip in 15 percent sulfuric acid, 15 percent hydrochloric acid, 70 percent water (by volume) with 6 to 10 grams of chromic acid added per 100 milliliters.
- ° Hot-water rinse.
- ° Air drying.

During cleaning, specimens were held in a basket fabricated from perforated molybdenum sheet. Thereafter, until welding was completed, specimens were handled only with tweezers or white gloves to prevent contamination.

A similar process would be applicable to TZM.

Unalloyed molybdenum was cleaned prior to welding as follows:⁽⁴⁴⁾

- ° Degrease with acetone.
- ° Immerse for 5 minutes in a 65-79°C (150-175°F) solution of 10 wt percent sodium hydroxide, 5 wt percent potassium permanganate, and 85 wt percent distilled water.
- ° Rinse in flowing tap water, brushing to remove smut.
- ° Immerse for 5-10 minutes in a room temperature solution of 15 vol. percent sulfuric acid, 15 vol. percent hydrochloric acid, 70 vol. percent distilled water plus 6-10 percent chromium trioxide.
- ° Rinse in tap water.
- ° Rinse with distilled water.
- ° Dry with hot air.

The following procedure was used to prepare TZM surfaces for diffusion bonding studies.⁽⁵²⁾

<u>PROCEDURE</u>	<u>COMMENTS</u>
1. Abrade with 3/0 emery paper	Perpendicular to bond width
2. Degrease in constant temperature, Pennsalt 45 solution	3 to 4 minutes
3. Rinse in distilled water	Room temperature
4. Immerse in complex acid etch for 5 minutes	95 cc H ₂ SO ₄ , 18.8 gm/1000 cc CrO ₃ 4.5 cc HNO ₃ 0.5 cc HF
5. Immerse in "Ryan" etch for 5 minutes.	
6. Rinse in distilled water	Room temperature
7. Dry with bottled nitrogen	Blast nozzle used

8.0 THERMAL PROCESSING

The thermal processing during fabrication of molybdenum and its alloys consists primarily of stress-relief annealing.

Stresses induced by forming or drawing can be relieved by heating in a protective atmosphere. The recommended temperature for unalloyed molybdenum is 870 to 980°C (1600 to 1800°F); the metal should be held at this temperature for limited time only, 1/4 to 1 hour. This limit should not be exceeded because recrystallization will begin and embrittlement might occur, regardless of the type of heating or the type of atmosphere. TZM is stress relieved at 1090 to 1260°C (2000 to 2300°F). Molybdenum can be stress-relieved at a lower temperature which requires a longer time at heat. The lowest recommended temperature is 725°C (1337°F)^(1, 11, 13)

The atmospheres used for heating the work pieces are described in the heating section of Section 5.1.

9.0 COATINGS

Coatings for the refractory metals may be considered in the design of the first wall of CTR's because they could possibly provide a desirable low Z number surface which would lessen the problems encountered with sputtered impurities. Also, the coatings may provide protection of the first wall from contamination by long term exposure to tramp interstitial elements (C, O, H, N) in the coolant.

There is a paucity of available data such as vacuum stability at temperature, of coatings exposed to the environment of a CTR. The type of coatings available now can be classified into two general categories, as (a) an oxidation resistant material applied to the refractory metal for protection and (b) a material applied to the refractory metal that reacts with the refractory substrate to form an oxidation-resistant layer. An example of the former would be noble metals; examples of the latter are aluminides and silicides. All coating processes on molybdenum must be performed below the recrystallization temperature of the alloy.

The methods available for coating application are presented in the following paragraphs.⁽⁵⁵⁾

9.1 Pack Processing

Pack coating involves immersion of the material to be coated in a granular pack medium, and a thermal cycle which is performed in a non-oxidizing environment. The coating is formed by vapor transport and diffusion. For the refractory metals, several promising coating systems are pack-applied; and, for the limited requirements for coated refractory metals to date, adequate coating facilities are generally available. Only experimental or low production quantities of coated aerospace and aircraft gas-turbine components have been required; consequently, little impetus has been provided for establishing reproducible and reliable production coating methods. Should demand for production coating of refractory metal components arise, a major effort would be required to advance current processes to the required technological level. Silicides are the principal

coatings that are pack-applied to refractory metals. An unresolved problem is reliable repair methods for pack-applied silicide coatings.

9.2 Slurry Processes

Slurry coating entails the application of a slurry mixture containing the coating elements on a substrate surface, generally by dipping or spraying, followed by a thermal treatment in a protective environment. Coating formation is achieved by vapor transport, liquid reaction, or solid-state sintering. Slurry processes have been widely used for the formation of high-temperature coatings on refractory metals, e.g., aluminides, silicides, and noble metals. A problem with slurry-applied coatings has been thickness control. From a manufacturing capacity standpoint, the lack of significant requirements for coated refractory metals to date precluded the need for expanded manufacturing capabilities.

9.3 Chemical Vapor Deposition

Chemical vapor deposition (CVD) is an entirely gaseous process in which the coating elements are transported to the substrate surface in vapor form and are deposited on the surface by chemical or pyrolytic reduction of the gaseous compound. This process has been successfully employed to apply many high-temperature protective coatings; however, the available facilities are predominately of laboratory scale. Substantial problems are encountered in depositing uniform coatings on complex shapes by CVD. Until a demand exists, and significant advantages are defined for CVD deposition of certain coatings, a specific effort aimed at developing expanded CVD manufacturing capabilities is not warranted.

An immediate problem in the aerospace field where CVD may be applicable is the deposition of a tungsten barrier layer coating on tantalum alloys.

9.4 Electrolytic Deposition

Electrolytic deposition includes conventional aqueous electroplating, electrolytic deposition from fused-salt baths, and electrophoresis. The last-named technique involves deposition of charged particles from a

liquid suspension onto an oppositely charged substrate. Aqueous electroplating is not widely used for forming high-temperature coatings.

Electrolytic deposition from fused salts has been successfully employed on a laboratory scale for depositing many high-temperature coatings.

Electrophoresis provides a means of applying uniform slurry coatings to complex shapes. It is a promising approach to resolving the problem of uniformly and reproducibly applying slurry coatings to high-temperature materials. Fused-silicide coatings can be electrophoretically deposited.

9.5 Fluidized Bed

Fluidized bed processing involves immersion of the material to be coated in a fluidized granular medium of the coating elements or inert materials. Fluidization is accomplished with an inert or reducing gas and/or a gas containing a halide form of the coating species. The process is a variation of chemical vapor deposition. Facility expense and high operating costs are disadvantages of this technique.

9.6 Plasma and Flame Spray Processes

Coating deposition with arc plasma or gaseous fuel-oxygen flame torches has proved extremely successful for the application of hardfacing and wear-resistant materials. These techniques have not been used extensively for applying high-temperature protective coatings, owing to problems related to density, bonding, thickness control, cost, and so on.

9.7 Hot-Dipping

Hot-dip coatings are formed by immersion of the part to be coated in a molten bath containing coating elements. Hot-dipping has been widely used to apply coatings to ferrous and nickel-base alloys; however, the family of high-temperature coatings applicable to these materials are better formed by other methods.

9.8 Cladding

This process entails sandwiching a structural high-temperature material between surface layers of a protective high-temperature alloy. Edge closure is a major problem associated with the cladding application of high-temperature coatings; consequently, little effort has been directed to applying this approach to high-temperature coating development. For the refractory metals, very few protective systems are amenable to cladding application.

9.9 Vacuum Vapor Deposition

Vacuum vapor deposition encompasses all methods associated with the physical vaporization and deposition of coating materials. This process has been widely used for the deposition of thin-film coatings on such things as mirrors, ornaments, and reflectors. Recently, methods have been developed for the deposition of .09 mm (3.5 mil) thick high-temperature coatings on superalloys and refractory metal substrates. The flexibility of this method for depositing coatings not amenable to formation by conventional diffusion processes makes it attractive for further development. Since relatively expensive facilities are required, laboratory demonstration of the capabilities of this technique must be accomplished first.

PART II - NIOBIUM
NIOBIUM OVERVIEW

Many niobium alloys have been developed and used to various degrees. These alloys vary substantially in strength and fabricability. Generally the lower strength alloys are the more fabricable and are less sensitive to deviation from the preferred processing conditions (tolerant of off nominal fabrication conditions). In selecting a niobium alloy for CTR application, attention must be given to both strength and fabricability/manufacturing tolerance. In many cases, good fabricability/manufacturing tolerance is more important than small increases in strength.

Strength as a function of temperature is given in Figure II-1 for several alloys. Figure II-2 shows the effect of welding on the DBTT for these alloys. Comparing the two figures shows FS-85 to be as a relatively high strength alloy which is also tolerant of interstitial contamination picked up during welding. FS-85 also has good creep strength.

For this study we selected Nb-1Zr, C103 (Nb-10Hf-1Ti), and FS-85 (Nb-28Ta-10W-1Zr) alloys for major emphasis. These three alloys are commercially available and represent low, moderate and relatively high strength alloys and low, intermediate and high alloy contents. Alloy composition may be important from a neutronics/radiation damage/activation standpoint. However, some of the detail fabrication data was not available for these 3 alloys; therefore, the data available for other alloys is also presented. These 3 selected alloys and essentially all "modern" niobium alloys have DBTT's well below room temperature when in the normally used annealed condition.

Interstitial contamination by carbon, oxygen, hydrogen, or nitrogen raises the DBTT considerably above room temperature. This fact necessitates extreme cleanliness when performing any elevated temperature operations such as welding, brazing, stress-relieving, or annealing. Significant contamination will result in brittle behavior in a component or structure

The following sections discuss the fabrication processes used for niobium and its alloys. It includes the procedures found that have proved

FIGURE II-1. ULTIMATE STRENGTH-TO-DENSITY RATIO OF UNCOATED, ANNEALED NIOBIUM ALLOYS

II-3

FIGURE II-2. DUCTILE-TO-BRITTLE TRANSITION TEMPERATURE
FOR ANNEALED NIOBIUM ALLOYS

satisfactory for fabricating rather complex structures. Examples of two McDonnell fabricated structures are shown in Figures II-3 and II-4. The fin and rudder, Figure II-3, were fabricated from F48 alloy, which was an early high strength, difficult to fabricate, alloy. Figure II-4 is an internal view of the structural cylinder for BGRV. The corrugated, EB welded cylinder, 81.28 cm (32 inches) in diameter and 147.32 cm (58 inches) long, was fabricated from Cb-752 alloy.

NIOBIUM FIN AND RUDDER

(F-48, Nb-15W-5Mo-1Zr)

FIGURE II-3. NIOBIUM FIN AND RUDDER, Nb-15W-5Mo-1Zr (F-48)

FIGURE II-4. NIOBIUM STRUCTURAL CYLINDER, EXTENSIVELY EB WELDED
417.3 CM X 81.3 CM DIAMETER (58 X 32 INCHES)

1.0 INSPECTION

The inspection of the moderate strength - high ductility niobium alloys is less complicated than that of molybdenum alloys.

An important inspection requirement for niobium and its alloys are the amounts of interstitial elements (C, O, H, N) present. When interstitial content is too high the material behaves in a brittle manner. There has been concern in the past that analytical techniques and standards for determination of the interstitials is inadequate to the extent that agreement on the analysis from different laboratories is difficult. With present analytical techniques it is doubtful that this would present a problem. The maximum interstitial limits for finished products are generally as follows: Carbon - 100 ppm; Oxygen - 300 to 400 ppm; Hydrogen - 10 to 15 ppm; and Nitrogen - 100 ppm. Future limits may be dictated by compatibility requirements.

A Wah Chang specification for Niobium alloys is included (Appendix B) as a representative specification for a niobium alloy.

2.0 BLANKING

The conventional blanking processes are applicable to the niobium alloys of interest and may be performed at room temperature.

Niobium alloys can be blanked, punched, and stamped at room temperature using steel dies with a 6% clearance^(13, 56, 57, 58, 59). Sawing and shearing can be used to blank the niobium alloys. Parameters for power hack sawing and band sawing with high speed steel blades as recommended in the Machinability Data Handbook⁽²³⁾ are as follows: (1) hack sawing - for material less than 19.05 mm (3/4 inch) thick use 3.9 teeth per cm (10 teeth per inch), 50 strokes/minute and a feed of .10 mm (0.004 inch)/stroke, (2) band sawing - for material less than 12.7 mm (1/2 inch) thick use a precision toothed blade with 5.5 teeth per cm (14 teeth per inch) and a band speed of 42.7 m (140 ft)/min. Acceptable results of shearing D-31 using a .050 (.002 inch) gap setting was reported by Trabold and Bank⁽⁶⁰⁾. They noted an "unusual serrated edge," how-

ever, no cracks were visible in metallographic analysis. They recommended deburring to a depth of at least .05 mm (0.002 inch) to remove the serrated edge. Neff and Frank⁽²⁵⁾ indicated no difficulty in shearing Nb-1Zr alloy.

Electrochemical machining or chemical blanking can be used, however, these operations may require a high temperature vacuum anneal to remove absorbed hydrogen in order to prevent hydrogen embrittlement of the niobium alloys.⁽⁵⁶⁾

Care must be exercised during blanking and all other operations to prevent gouging or scratching of the niobium alloys.⁽³⁾

3.0 EDGE PREPARATION

Edge preparation or deburring may be accomplished using conventional techniques, unlike molybdenum, delamination is not a problem. Hand filing and vibrating radiusing similar to that discussed for molybdenum are most often used. Vibratory radiusing is accomplished at frequencies of 1400 to 1800 cycles/minute. Edge grinding is possible but because of the softness, especially in the annealed condition, niobium alloys tend to rapidly load the grinding wheels or discs.^(13, 18, 55)

4.0 MACHINING

Niobium base alloys can be machined using standard machining practices. Depending upon the specific alloy content, niobium and its alloys have machining characteristics that vary from those of soft copper to annealed stainless steel. The machining characteristics of the highly alloyed niobium alloys of interest are intermediate to those of the soft and gummy low tantalum alloys and the brittle, abrasive molybdenum alloys. The relative softness of niobium alloys causes smearing and buildup of material on the cutting edge which is a problem to chip formation. Because of the softness and its related difficulties, the niobium alloys are generally considered unsuitable for grinding.

Rigid tooling is recommended for optimum machining. Workpiece deflection problems encountered would approximate those experienced when machining titanium alloys.

High speed steel (HSS) tools may be used for all machining operations; however, carbide tools are frequently used, especially for single point cutting and face milling. The work should be flooded with a soluble oil, oils containing chlorine or sulfur, carbon tetrachloride or trichloroethylene.^(13, 16, 19, 20, 21, 56, 57, 58, 61, 62, 65)

4.1 Face Milling

The major difficulty encountered in face milling niobium alloys is that of base metal buildup on the cutting edges of the tools. As a result, the usable range of cutting speeds for carbide tools approaches that of high speed steel tools. For D-31 alloy, Stewart and Arzt⁽²¹⁾ report good performance with standard geometry HSS cutters at cutting speeds of 30.5 to 38.1 m/min (100 and 125 ft/min). Carbide cutters must be specially ground with highly-positive rake angles to achieve reasonable tool life at speeds of 45.7 m (150 ft)/min. When using high speed steel tools, the D-31 responded readily to changes in basic machining conditions. The use of large radial rake angles, premium grades of tool material, and a highly chlorinated cutting oil will enhance tool life or increase allowable cutting speed.

Face milling of Nb-1Zr with an M-2 HSS 5.08cm (2-inch) diameter 8 flute end mill cutting on the end of the tool was reported by Neff and Frank.⁽²⁵⁾ The speed was 15.2 m (50 ft)/min with a feed of .56 mm (0.022 inch) per tooth; depth of cut was 1.27 mm (0.050 inch); coolant was sulfurized mineral oil 1:1. These cutting conditions produced poor surface finish and chip formation. The milling parameters used in this small study differ significantly from those recommended by the Machining Data Handbook, which may explain the rather poor results.

The basic face milling recommendations are presented in Table II-1.

TABLE II-1. FACE MILLING RECOMMENDATIONS FOR NIOBIUM ALLOYS

FEEDS AND SPEEDS

HARDNESS BHN	CONDITION	DEPTH* OF CUT mm (inches)	HIGH SPEED STEEL TOOL			CARBIDE TOOL			
			SPEED m/min (fpm)	FEED mm/tooth (in./tooth)	TOOL MATERIAL	SPEED - m/min (fpm)		FEED mm/tooth (in./tooth)	TOOL MATERIAL
						BRAZED	THROW- AWAY		
170 to 225	Stress Relieved	2.54 (.100)	36.6 (120)	.254 (.010)	T15, M33, M41 Thru M47	42.7 (140)	47.2 (155)	.254 (.010)	C-2
		.38 (.015)	48.8 (160)	.20 (.008)	T15, M33, M41 Thru M47	45.7 (150)	50.3 (165)	.20 (.008)	C-2

TOOL GEOMETRY

HARDNESS BHN	HIGH SPEED STEEL		THROWAWAY CARBIDE		BRAZED CARBIDE		CORNER ANGLE degrees	END CUTTING EDGE ANGLE degrees	AXIAL RELIEF ANGLE degrees	RADIAL RELIEF ANGLE degrees
	AXIAL RAKE ANGLE degrees	RADIAL RAKE ANGLE degrees	AXIAL RAKE ANGLE degrees	RADIAL RAKE ANGLE degrees	AXIAL RAKE ANGLE degrees	RADIAL RAKE ANGLE degrees				
170-225	0	20	5 to 7	0 to 5	0	10	45	5 to 10	10	10

4.2 End Milling

Very good tool life, metal removal rates, and surface finish are obtainable when using standard high speed steel cutters for slotting. Cutters made of M-2 grade were run at cutting speeds of 21.3 to 24.4 m/min (70-80 ft/min) with a feed rate of .076 mm (0.003 inch) per tooth; 30.5-33.5 m/min (100-110 ft/min) with a feed rate of .050 (0.002 inch) per tooth on D-31 alloy⁽²¹⁾ and 26.8 m/min (88 ft/min) with a feed rate of .025 (0.001 inch)/tooth on Nb-1Zr alloy.⁽²⁵⁾ Stewart and Arzt⁽²¹⁾ report a 30% increase in allowable cutting speed when T-15 HSS were used on D-31 alloy. Trabold and Banks⁽⁶⁰⁾ report that speeds of 9.8 to 28 m/min (32 to 92 surface ft/min) .127 to .050 mm (0.005 to 0.002 inch) chip loads gave the best results and maintained a 40 to 60 rms surface finish when end milling D-31. The tool was a 44.5 mm (1-3/4 inch) diameter, 6 flute, right-spiral, right-hand cut, HSS cutter. The speeds used during these successful operations are slower than those recommended in the Machining Data Handbook⁽²³⁾ shown in Table II-2. Chlorinated or sulpho-chlorinated cutting oils provide substantially better results than do water soluble fluids.^(21, 61)

The basic end milling recommendations for niobium are presented in Table II-2. The basic side and slot milling recommendations are presented in Table II-3.

4.3 Turning

The niobium alloys of interest can be turned using HSS or carbide tools. There was general agreement on the parameters reported for turning D-31⁽²¹⁾ and Nb-1Zr⁽²⁵⁾ with the parameters recommended in the Machining Data Handbook shown in Table II-4. Tool geometry is perhaps the most important single factor to consider when turning the niobium alloys.^(21, 61) Turning has been performed dry as well as with sulfurized mineral oil and water soluble oil.

The basic turning recommendations are presented in Table II-4.

TABLE II-2. END MILLING RECOMMENDATIONS FOR NIOBIUM ALLOYS
FEEDS AND SPEEDS

Peripheral

HARD- NESS BHN	CONDITION	DEPTH OF CUT mm (inches)	HIGH SPEED STEEL TOOL						CARBIDE TOOL					
			SPEED m/min (fpm)	FEED – mm(inches) per Tooth				TOOL MTL	SPEED m/min (fpm)	FEED – mm (inches) per Tooth				TOOL MTL
				CUTTER DIAMETER mm (inches)						CUTTER DIAMETER mm (inches)				
				6.35 (1/4)	12.7 (1/2)	19.05 (3/4)	25 to 50 (1 to 2)			6.35 (1/4)	12.7 (1/2)	19.05 (3/4)	25 to 50 (1 to 2)	
170 to 225	Stress Relieved	1.27 (.050)	24.3 (80)	.050 (.002)	.075 (.003)	.075 (.003)	.100 (.004)	T15*	45.7 (150)	.050 (.002)	.075 (.003)	.075 (.003)	.100 (.004)	C-2
		.38 (.015)	30.5 (100)	.038 (.0015)	.050 (.002)	.063 (.0025)	.075 (.003)	T15*	53.3 (175)	.038 (.0015)	.050 (.002)	.063 (.0025)	.075 (.003)	C-2

Slotting

HARDNESS BHN	CONDITION	DEPTH* OF CUT mm (inches)	SPEED m/min (fpm)	FEED – mm (inches) per Revolution				HSS TOOL MATERIAL except as noted
				NOMINAL HOLE DIAMETER – mm (inches)				
				6.35 (1/4)	12.7 (1/2)	19.05 (3/4)	25 to 50 (1 to 2)	
170 to 225	Stress Relieved	6.35 (.250)	9.1 (50)	–	–	.050 (.002)	.075 (.003)	M15, M33, M41 thru M47
		1.27 (.050)	10.7 (55)	.017 (.0007)	.025 (.001)	.038 (.0015)	.050 (.002)	

TOOL GEOMETRY

HARDNESS BHN	HELIX ANGLE degrees	RADIAL RAKE ANGLE degrees	END CUTTING EDGE CONCAVITY ANGLE degrees	AXIAL RELIEF ANGLE degrees	RADIAL† RELIEF ANGLE degrees
170-290	30	10	3 to 7	3 to 7	C

†Radial Relief Angles for Various Size End Mills:

Size*	3.18 (1/8)	4.76 (3/16)	6.35 (1/4)	9.52 (3/8)	12.7 (1/2)	19.05 (3/4)	25.4 (1)	38.1 (1-1/2)
C	19	19	15	13	13	12	10	8

*UNITS - mm (in.)

TABLE II-3. SIDE AND SLOT MILLING RECOMMENDATIONS
FOR NIOBIUM ALLOYS. (ARBOR MOUNTED CUTTERS)

FEEDS AND SPEEDS

HARDNESS BHN	CONDITION	DEPTH* OF CUT mm (inches)	HIGH SPEED STEEL TOOL			CARBIDE TOOL		
			SPEED m/min (fpm)	FEED mm/tooth (in./tooth)	TOOL MATERIAL	SPEED m/min (fpm)	FEED mm/tooth (in./tooth)	TOOL MATERIAL
170 to 225	Stress Relieved	6.35 (.250)	36.6 (120)	.127 (.005)	T15, M33, M41 Thru M47	41.1 (135)	.127 (.005)	C-2
		1.27 (.050)	41.1 (135)	.178 (.007)	T15, M33, M41 Thru M47	45.7 (150)	.178 (.007)	C-2

TOOL GEOMETRY

HARDNESS BHN	HIGH SPEED STEEL				CARBIDE			
	AXIAL RAKE ANGLE degrees	RADIAL RAKE ANGLE degrees	AXIAL RELIEF ANGLE degrees	RADIAL RELIEF ANGLE degrees	AXIAL RAKE ANGLE degrees	RADIAL RAKE ANGLE degrees	AXIAL RELIEF ANGLE degrees	RADIAL RELIEF ANGLE degrees
170-290	0	15 to 20	3 to 5	5 to 10	0	5 to 15	7 to 10	7 to 10

TABLE II-4. TURNING RECOMMENDATIONS FOR NIOBIUM ALLOYS

FEEDS AND SPEEDS

HARDNESS BHN	CONDITION	DEPTH* OF CUT mm (inches)	HIGH SPEED STEEL TOOL			CAST ALLOY TOOL		CARBIDE TOOL			
			SPEED m/min (fpm)	FEED mm/rev (in./rev)	TOOL MATERIAL	SPEED m/min (fpm)	FEED mm/rev (ipr)	SPEED - m/min (fpm)		FEED mm/rev (in./rev)	TOOL MATERIAL
								BRAZED	THROW- AWAY		
170 to 225	Stress Relieved	2.54 (.100)	21.3 (70)	.127 (.005)	M2, M3	30.5 (100)	.127 (.005)	80.8 (265)	-	.127 (.005)	C-2
		.38 (.015)	27.4 (90)	.127 (.005)	M2, M3	42.7 (140)	.127 (.005)	97.5 (320)	-	.127 (.005)	C-2

TOOL GEOMETRY

NOTE: ALL RAKE AND RELIEF ANGLES ARE
MEASURED IN NORMAL DIRECTION.

HARDNESS BHN	HIGH SPEED STEEL AND CAST ALLOY TOOL					CARBIDE TOOLS						
	BACK RAKE ANGLE degrees	SIDE RAKE ANGLE degrees	END RELIEF ANGLE degrees	SIDE RELIEF ANGLE degrees	SIDE AND END CUTTING EDGE ANGLE degrees	BRAZED		THROWAWAY		END RELIEF ANGLE degrees	SIDE RELIEF ANGLE degrees	SIDE AND END CUTTING EDGE ANGLE degrees
						BACK RAKE ANGLE degrees	SIDE RAKE ANGLE degrees	BACK RAKE ANGLE degrees	SIDE RAKE ANGLE degrees			
170-290	0	20	5	5	5	0	20	-	-	5	5	15

4.4 Drilling

The drilling characteristics of the niobium alloys are strongly influenced by the abrasiveness of the particular alloy composition. Split point drills have been used most in drilling in order to minimize rubbing and accelerated wear at the drill margins.^(21, 25, 60) Neff and Frank⁽²⁵⁾ reported drilling 5.15 mm (0.203 inch) diameter holes in Nb-1Zr using HSS cobalt drills with 118° split point drills. The feed was 14.6 m (48 ft)/min with a feed of .038 mm (0.0015 inch)/rev. Stewart and Arzt⁽²¹⁾, in their studies on D-31, used split point drills, cutting speeds of 24.4 to 30.4 m (80 to 100 ft)/min and a feed of .050 mm (0.002 inch)/rev. Highly active sulfurized or chlorinated cutting oils are recommended. Chattering may develop if a soluble oil is used.

The basic drilling recommendations are presented in Table II-6.

4.5 Grinding

The niobium alloys are difficult to grind. The wheel rapidly wears and becomes loaded. The wheels must be dressed often and flooded with a grinding fluid. A water solution with KNO_2 has been reported best, at least for the D-31 alloy. Aluminum oxide wheels of J or K hardness and wheel speeds between 609 and 1219 m (2000 and 4000 ft)/min are satisfactory. High table speeds 18.2 m/min (60 ft/min) in combination with low down feeds .0127 mm/pass (0.0005 in/pass) and low cross feeds .63 mm/pass (0.025 in/pass) give satisfactory metal removal rates and surface finish.^(21, 57, 66, 67)

The basic surface grinding recommendations are presented in Table II-5.

TABLE II-5. SURFACE GRINDING RECOMMENDATIONS.

HARDNESS BHN	CONDITION	WHEEL SPEED m/min (fpm)	TABLE SPEED m/min (fpm)	DOWNFEED mm(in.)/pass	CROSSFEED mm(in.)/pass	WHEEL
170 to 225	Stress Relieved	1219 (4000)	15 to 30 (50 to 100)	Rough .025 (.001) Finish .012(.0005) max.	.050-5.08 (.020-.200) (Max: 1/12 of Wheel Width)	A46JV

TABLE II-6. DRILLING RECOMMENDATIONS FOR NIOBIUM ALLOYS

FEEDS AND SPEEDS

HARDNESS BHN	CONDITION	SPEED m/min (fpm)	FEED – mm (inches) per Revolution				HSS TOOL MATERIAL except as noted
			NOMINAL HOLE DIAMETER – mm (inches)				
			1.58 (1/16)	3.17 (1/8)	6.35 (1/4)	12.70 (1/2)	
170 to 225	Stress Relieved	9.1 (50) 24.3 (80)	.025 (.001) —	.075 (.003)	.127 (.005)	.170 (.007)	M15, M33, M41 thru M47

TOOL GEOMETRY

High Speed Steel Twist

HARDNESS BHN	POINT ANGLE degrees	LIP RELIEF ANGLE degrees	CHISEL EDGE ANGLE degrees	HELIX ANGLE degrees	POINT GRIND
170-290	118	7 to 10	125 to 135	24 to 32	Standard

4.6 Chemical Milling

Procedures have been developed for metal removal by chemical milling using a HNO_3 -HF solution; however the composition is proprietary.⁽¹⁰⁰⁾ There is a possibility of hydrogen pickup in the niobium alloys. A high temperature vacuum anneal may be required to remove excessive hydrogen in order to prevent hydrogen embrittlement.

5.0 FORMING

Niobium and its alloys are generally fabricated in the fully recrystallized, equiaxed, fine grain size condition. The annealed niobium alloys tend to behave like mild steel except that they have a greater tendency to gall, seize and tear during forming, and require precautions to avoid these difficulties. Fabrication is usually done at room temperature, but warm forming at 426°C (800°F), if required, may be accomplished without protective coatings. Die materials and lubricants have been developed for niobium alloys to minimize or eliminate the galling of the material with the die. In some operations such as deep drawing, aluminum bronze dies are commonly used, although the punches can be steel unless slippage occurs. For operations like form stamping the dies are generally steel except in cases of severe slippage, where aluminum bronze or beryllium copper dies should be used. Low melting alloys are sometimes used for short runs. Ordinary oils and greases are commonly used lubricants for forming of niobium alloys, since these materials are generally formed at room temperature. For severe forming operations, petrolatum is frequently used. A backup sheet is often used in press brake operations to reduce galling and to provide support so that the part will more closely follow the punch radius.⁽⁶⁸⁾

Work hardening of the stronger alloys results in the need for intermediate annealing after severe forming.

The interstitial elements, carbon, nitrogen, hydrogen and especially oxygen even in small amounts can severely embrittle niobium alloys, so the materials should be kept as clean as possible to insure good formability. Lack of such precautions can result in failures during fabrication. The most

common causes of surface contamination are failure to clean the surface properly before annealing, and failure to provide an adequately good vacuum (low absolute pressure and low leak rate) in the vacuum annealing operation. Generally, the higher strength alloys are more severely embrittled by surface contamination than are the lower strength alloys.⁽⁶⁸⁾

Forming of niobium alloys has been accomplished successfully by a number of commonly used secondary fabrication techniques.^(3, 13, 16, 17, 25, 26, 29, 35, 36, 56, 57, 59, 62, 65, 68, 69) These methods include closed die forging, extrusion, form spinning, shear spinning (flow-turning), and extrusion spinning employed singly or in combination to fabricate plates, sheets or tubular blanks. Niobium and its alloys can be blanked, punched, stamped, and deep drawn at room temperature by hydroforming or in steel dies using a 6% clearance.

Neff and Frank⁽²⁵⁾ reported forming studies on F-48 and Nb-1Zr alloys. The F-48, because of its high W and molybdenum content, behaves in a more brittle manner than the lower strength Nb-1Zr alloy. Therefore, the F-48 was formed at elevated temperatures up to 371°C (700°F) using standard dies. Precautions similar to those necessary when forming molybdenum were exercised. The Nb-1Zr can be formed at room temperature with little difficulty.

Stratton et al⁽³⁾ report that for the X-20 program, room temperature was recommended for forming FS-82 and D-36, although temperatures up to 121°C (250°F) were permitted. The review of the literature did not reveal detailed procedures for forming the niobium alloys of interest. These alloys have been used successfully to fabricate components for aerospace applications. C-103 has been used in the Apollo program in the Lunar Excursion Module (LEM) descent engine and the Apollo Service Module Engine for restart operation in space. FS-85 has been used to fabricate panels for the evaluation studies on the Space Shuttle Supplementary Structural Test Program. The reports do not describe any difficulties during forming, therefore one would expect few difficulties in forming these alloys.

The formability curves and tables reported by Wood, et al⁽³⁾ used Cb-752 as a test material, therefore these have been included in this report for reference purposes. The niobium alloys of interest in this report should show better formability.

5.1 Brake Forming

The simplest type of forming operation whereby sheet metal is bent to form straight sections such as angles and channels.

The process types are air and die bending. In air bending, the work-piece is supported at its outer edges only and the length of the ram stroke determines the fast angle α . See Figure II-5.

The optimum forming temperatures for brake forming as reported by Wood⁽³⁰⁾ are shown in Figure II-6. As indicated by the formability index, the optimum temperature for brake forming is room temperature. This corresponds to general literature that most forming is performed at room temperature.

FIGURE II-5. BRAKE FORMING PROCESSES

FIGURE II-6. OPTIMUM FORMING TEMPERATURE CURVES FOR BRAKE FORMING

The forming limit table, Table II-7, can be used as follows:

1. Determine the bend angle (α), the material thickness (T), and the direction of bending, i.e., either longitudinal (L) or transverse (T).
2. Compare the bend angle required to the critical bend angle.
Case 1: If the known bend angle is greater than the critical bend angle, then the bending limits are the same as the tabulated critical bending limits.
Case 2: If the known bend angle is less than the critical bend angle, interpolate the tabulated R/T ratios and the various angles (α) below critical to determine the required R/T ratio.
3. Multiply the bending limit (R, T) by the material thickness (T) to determine the minimum radius of bend (R).

The formability envelope is shown in Figure II-7. Theoretically, all formable parts are limited to the area above the curve.

5.2 Joggling

Neff and Frank ⁽²⁵⁾ reported some cracking during joggling the F-48 alloy. Forming was accomplished at 315°C (600°F). This, however, is an obsolete alloy having a DBTT above room temperature.

The theoretical formability curve for joggling by Wood ⁽³¹⁾ is shown in Figure II-8. This is for the D31 (10 Mo-10 Ti-Nb) alloy.

5.3 Beading

The rubber forming beaded panel forming limits derived by Wood et al ⁽³⁰⁾ is shown in Table II-8. These limits are based on a 20.7 MPa (3000 psi) maximum forming pressure. Instructions for using the table are as follows:

1. Calculate L/T ratio from given dimensions.
2. Compare the known L/T with the tabulated critical L/T.

Case 1: If the known L/T is less than the critical L/T, then the maximum bend radius (R Max.) obtained will be due to insufficient pressure 20.7 MPa (3000 psi). Interpolate the tabulated L/T values and corresponding R/L values for insufficient pressure to determine the required R/L ratio. Multiply R/L

TABLE II-7. FORMING LIMITS FOR BRAKE BENDING

Material	Grain Direction	Bending Temperature °C °F	Critical Bend α°	Critical Bend Limits R/T	Bending Limits (R/T)						
					For Various Angles (α) Below Critical						
					30	45	60	75	90	105	120
2024-T3	L	R.T. R.T.	111	2.02	.50	.90	1.38	1.70	1.90	2.0	2.0
TZM MoLy	L	R.T. R.T.	121	1.12	.30	.55	.81	.98	1.10	1.12	1.12
Cb-752	L	R.T. R.T.	121	1.20	.38	.60	.85	1.05	1.18	1.20	1.20
2024-T3	L	315 600	122	1.07	.17	.28	.45	.75	1.00	1.15	1.18
PH 15-7 Mo	L	1038 1900	126	.65	.05	.08	.12	.20	.38	.55	.63
TZM MoLy	L	482 900	118	1.40	.10	.20	.25	.30	.50	1.10	1.40
Cb-752	L	482 900	115	2.00	.15	.20	.40	.75	1.30	1.80	2.00

FIGURE II-7. BENDING FORMABILITY ENVELOPE

FIGURE II-8. COMPOSITE GRAPH FOR JOGGLING

TABLE II-8. RUBBER FORMING BEADED PANEL FORMING LIMITS

PART SHAPE AND PARAMETERS

Insufficient Pressure Limits (R/L)				Splitting Limits (R/T)			
Material	Critical Rate L/T	Temp. °C	Temp. °F	For R/T Ratios of		For R/L Ratios of	
				2	5	.01	.03
Cb-752	160	R.T.	R.T.	R/L .093	.123	R/T 60	54
				L/T 21.5	40.6	L/T 6000	1800
Cb-752	129	538	1000	R/L .110	.143	R/T 60	54
				L/T 18.2	34.9	L/T 6000	1800

by the distance between bead centers (L) to determine the maximum bead radius (R Max.).

Case 2: If the known L/T is greater than the critical L/T, interpolate the tabulated L/T ratios and corresponding R/T values for splitting to determine the required R/T ratio. Multiply R/T by the material thickness (T) to determine the maximum bead radius (R Max.).

The theoretical limit curves for drop hammer beading are presented in Figure II-9.

5.4 Dimpling

The forming limit tables by Wood ⁽³⁰⁾ are presented in Table II-9. The instructions for using the tables are as follows:

1. Determine bend angle (α) and hole radius (R) required.
2. Compare known bend angle (α) with the tabulated bend angle.

Case 1: If the known bend angle is tabulated, read the corresponding H/R value.

Case 2: If the known bend angle is not tabulated, interpolate the tabulated α and corresponding H/R ratios for splitting to determine the required H/R value.

3. Multiply H/R by the hole radius (R) to determine the length of dimple flange (H).

5.5 Hydroforming

Rubber Forming - A method of die forming sheet metal where rubber is normally used as the female die; principally used for flanging and shallow recessing. There are two process types, single and double action. In the single action process the forming pressure is exerted from only one direction, whereas in the double action process the pressure is applied from two directions. These are shown schematically in Figure I-19.

The rubber forming shrink flange limits ⁽³⁰⁾ are presented in Table II-10. The instructions for using the table are as follows:

1. Calculate R_D/T ratio from given dimensions.
2. Compare the known R_D/T with the tabulated critical R_D/T .

FIGURE II-9. COMPOSITE OF OPTIMUM DROP HANGER LIMIT CURVES IN THE ROOM TEMPERATURE TO 315°C RANGE.

TABLE II-9. DIMPLING LIMITS
(RADIAL SPLITTING AT EDGE OF HOLE)

Material	Dimpling Limits (H/R)						
	Dimpling Temperature		For Various Bend Angles (α)				
			Above and Below Standard Bend Angle				
	$^{\circ}\text{C}$	$^{\circ}\text{F}$	30 $^{\circ}$	35 $^{\circ}$	Standard 40 $^{\circ}$	45 $^{\circ}$	50 $^{\circ}$
2024-T3	R.T.	R.T.	2.15	1.60	1.20	.93	.80
TZM Moly	R.T.	R.T.	1.98	1.50	1.12	.87	.73
Cb-752	R.T.	R.T.	2.28	1.70	1.30	.98	.83
PH 15-7 Mo 260	260	500	2.43	1.84	1.40	1.07	.90

PART SHAPE AND PARAMETERS

TABLE II-10. RUBBER FORMING SHRINK FLANGE LIMITS

Material	Temperature °C	Pressure Limits H/T	Critical Ratio R_D/T	$\frac{H}{R}$ $T - H/R$	Elastic Buckling Limits - (H/T)											
					For Various (H/R) Ratios											
					.001	.002	.005	.007	.010	.015	.020					
					R_D/T	H/T	R_D/T	H/T	R_D/T	H/T	R_D/T	H/T	R_D/T	H/T	R_D/T	H/T
2024-T3	R.T.	7.4	469	.029	R.T.	69,930	70	24,950	50	6368	32	3833	27	2277	23	1249
Ti-8-1-1	R.T.	9.5	2143	.008	R.T.	47,952	48	16,966	34	4378	22	2621	18			
TZM Mo1y	R.T.	8.8	1576	.015	R.T.	91,908	92	32,435	65	8358	42	5114	36	2970	30	1606
Cb 752	R.T.	6.6	892	.024	R.T.	67,930	70	24,950	50	6368	82	3833	27	2277	23	1248
															17	784
															16

- Case 1: If the known R_D/T is less than the critical R_D/T , multiply K times R_D to determine the maximum flange height (H Max.).
- Case 2: If the known R_D/T is greater than the critical R_D/T , interpolate the tabulated R_D/T ratios and corresponding H/T values for buckling to determine the required H/T ratio. Multiply H/T by the material thickness (T) to determine the maximum flange height (H Max.).
3. Multiply the pressure limit (H/T) by the material thickness (T) to determine the minimum flange height (H Min.).

The rubber forming stretch flange limits ⁽³⁰⁾ are presented in Table II-11. The instructions for using these are the same as those above.

5.6 Spinning

Spinning is a very popular and satisfactory method of forming niobium and its alloys into symmetrical sheet metal parts. The advantages of the spinning process are low tooling costs, short setup times, and relatively close dimensional tolerances.

There is no unanimous consensus as to the temperature at which the spinning operations be performed. Some early published articles indicate elevated temperatures may be required, whereas more recent articles indicate that room temperature forming may be performed. The optimum spin forming temperature curves of Wood, et al ⁽³⁰⁾ are shown in Figure II-10. These indicate that room temperature is applicable at least for the CB 752 alloy.

Lubrication is necessary to prevent galling of the workpiece by the forming tools. Molybdenum disulfide or graphite can be used as lubricants. ^(56, 16, 64)

The spin forming limits tables by Wood ⁽³⁰⁾ are presented in Table II-12. Instructions for using these tables are as follows:

1. Calculate D_D/T ratio from given dimensions.

TABLE II-11. RUBBER FORMING STRETCH FLANGE LIMITS

Material	Temperature	Pressure Limits	Critical Ratio	$\frac{H/R}{1 + H/R}$		Buckling Limits (H/T) Above Critical											
						For Various (H/R) Ratios											
						.01		.02		.05		.10		.20		.30	
						R_D/T	H/T	R_D/T	H/T	R_D/T	H/T	R_D/T	H/T	R_D/T	H/T	R_D/T	H/T
2024-T3	R.T.	18	82	.28	R.T.	4343	43	1530	30	462	22	242	22	132	22	95	22
Ti-8-1-1	R.T.	14	138	.13	R.T.	3535	35	1275	25	378	18	204	18				
TZM Moly	R.T.	17	144	.19	R.T.	5555	55	1989	39	567	27	297	27	164	27		
TZM Moly	260	16	150	.19	R.T.	5858	58	2142	42	588	28	308	28	168	28		
Cb 752	R.T.	24	74	.32	R.T.	4848	48	1734	34	504	24	264	24	144	24	104	24

FIGURE II-10. RECOMMENDED FORMING TEMPERATURE
CURVES FOR SPINNING

Blank Diameter to Die Ratios (D_B/D_D) and Cup Depth Ratios (H/D_D)										
Material	Temperature °C	Material Gage mm (in.)	Ratio	For Various (D_D/T) Ratios						
				25	50	100	150	200	250	300 400
Cb-752	R.T.	.5 .020	D_B/D_D	1.48	1.50	1.34	1.26	1.21	1.18	1.16 1.12
			H/D_D	.38	.40	.17	.14	.12	.11	.10 .08
Cb-752	R.T.	1.0 .040	D_B/D_D	1.48	1.49	1.34	1.22	1.15		
			H/D_D	.38	.39	.26	.15	.10		
Cb-752	R.T.	1.6 .063	D_B/D_D	1.48	1.49	1.24	1.15			
			H/D_D	.39	.39	.18	.10			

TABLE II-12. SPINNING LIMIT TABLES (FLAT BOTTOM CYLINDRICAL CUPS)

2. Interpolate the D_D/T ratios and corresponding D_B/D and H/D_D values to determine the required D_B/D_D and H/D_D ratios. Multiply the required D_B/D_D value by the die diameter (D_D) to determine the maximum blank diameter (D_B). Multiply the required H/D_D by D_D to determine the maximum cup depth (H).

5.7 Drawing

The deep drawing forming limits reported by Wood et al ⁽³⁰⁾ are shown in Table II-13. Instructions for using these tables are as follows:

1. Calculate D_D/T ratio from given dimensions.
2. Interpolate the D_D/T ratios and corresponding D_B/D and H/D_D values to determine the required D_B/D_D and H/D_D ratios. Multiply the required D_B/D_D value by the die diameter (D_D) to determine the maximum blank diameter (D_B). Multiply the required H/D_D by D_D to determine the maximum cup depth (H).

5.8 Explosive Forming

Neff and Frank ⁽²⁵⁾ report successfully forming a beaded panel of .51mm (0.02 inch) thick Nb-1Zr alloy using the test setup shown in Figure II-11.

An explosive charge of 6.25 grams of primacord at 25.4 cm (10 inch) stand-off and 63.5 cm (25 inch) water head was used to form the niobium panel. A partial vacuum of 91.2 kPa (27 inches) of mercury was maintained between work piece and die cavity to eliminate air trap burns during forming. The charge was shaped to a 5.08 cm (2 inch) by 10.2 cm (4 inch) oval with a 4.4 cm (1-3/4 inch) cross piece of primacord at the oval center. The #6 electrical blasting cap used to ignite the primacord was attached to the cross piece and the whole charge was centered over the work piece and die. This firing produced a panel with 3.3 mm (.13 inch) bead depth.

TABLE II-13. DEEP DRAWING WITH MECHANICAL (FLAT BOTTOM CYLINDRICAL CUPS)

Material	Temperature (°C) (°F)		Ratio	Die to Mark Diameter Ratios (D_B/D_D)							
				Cup Depth Ratios (H/D_D)							
				For Various D_D/T Ratios							
				25	50	100	150	200	250	300	400
Cb-752	R.T.	R.T.	D_B/D_D	1.91	1.96	1.78	1.61	1.43	1.43	1.37	1.30
			H/D_D	.64	.67	.57	.41	.31	.26	.22	.18
Cb-752	204	400	D_B/D_D	2.10	2.30	2.04	1.75	1.59	1.46	1.40	1.36
			H/D_D	.92	1.02	.76	.51	.38	.37	.32	.21

FIGURE 11-11. EXPLOSIVE FORMING SET-UP

6.0 JOINING

Niobium and its alloys can be joined by gas-tungsten-arc (GTA) or electron beam (EB) welding, resistance welding, diffusion bonding, and brazing techniques. The requirements and limitations, if any, for each method will be discussed.

6.1 Fusion Welding

A considerable number of investigations have been performed to evaluate fusion welding of niobium and its alloys^(1, 3, 11, 13, 17, 21, 26, 40, 56, 58, 59, 60, 61, 62, 65, 66, 71, 75, 76, 77, 78, 79, 81, 82, 83, 84, 85, 86, 88, 89, 90, 91, 92, 93, 94). The procedures are generally in agreement, and a few of them are summarized below.

The microstructural changes that occur due to fusion welding do not appear to present serious problems for the niobium alloys. All refractory alloys suffer some loss in ductility and increased DBTT when welded, but niobium alloys are less affected than molybdenum. The coarse grain size of the weld metal and of the heat-affected-zone along with the solution, precipitation, and aging of precipitates in some alloys, which result due to the thermal cycling during welding, can collectively cause a severe loss in ductility and increase the ductile-to-brittle transition temperature of the welds. The ductile-to-brittle transition temperature of essentially all of the niobium alloys is increased by fusion welding, but to different degrees in the different commercial alloys. Several detailed studies on welding have included the DBTT in their scope^(70, 71, 72, 73, 74, 75, 76, 77). Table II-14 shows some of the results⁽⁷⁰⁾.

Although preheating is not required for the niobium-base alloys, postweld annealing as shown in Table II-14, can restore a considerable amount of ductility to niobium-base alloys and can reduce the ductile-to-brittle transition temperature to some temperature lower than that of the as-welded material.

TABLE II-14. DUCTILE TO BRITTLE TRANSITION TEMPERATURE FOR MODERATE STRENGTH NIOBIUM ALLOYS

Alloy	Base Condition		1 Hr. Post Weld		DBTT, (a)°F					
	Final Heat Treatment	Grain Size ASTM	Anneal		Base Material		TIG Weld		EB Weld	
			°C	°F	Long/Trans	°C	°F	Long	°C	°F
	Time									
B-66		10	None	1038 1900	> -184 -300	< -171 -250	-18 0	24 75	-143 -225	-115 -175
C-129Y	1316 2400	10	1316 2400	1204 2200	< -196 -320	-129 -200	-143 -225	-171 -250	-171 -250	-171 -250
Cb-752	1204 2200	8-9	1204 2200	1316 2400	-171 -275	-59 -75	-18 0	-129 -200	-129 -200	-129 -200
D-43	1427 2600	5	1316 2400	1316 2400	> -101 -150	38 100	-18 0	-143 -225	-87 -125	-87 -125
FS-85	1302 2375	8	1316 2400	1204 2200	-171 -250	-115 -175	-115 -175	-129 -200	-129 -200	-129 -200

(a) 90° Bend Transition Temperature, 1T Bend Radius (FS-85, 2T Radius); Ram Speed 2.54 cm (1 inch)/min.

Contamination is the most probable difficulty that may be expected during fusion welding. Niobium and its alloys react with and absorb the interstitial impurities, carbon, oxygen, nitrogen, and hydrogen at temperatures above about 315°C (600°F). Since only a small amount of these impurities can produce severe embrittlement, it is mandatory that the area being welded is shielded from ambient atmosphere. The interstitial limits should be kept below 100 ppm for C; 400 ppm for O; 15 ppm for H; and 100 ppm for N.

The shielding of the area during welding can be accomplished in a vacuum chamber, as in EB welding, and by leading, trailing, and backup inert gas shields or in an inert atmosphere chamber for GTA welding.

Prior to welding, all details must be cleaned. The procedures generally require pickling in an HNO_3 -HF or HNO_3 -HF- H_2SO_4 solution and may also include a final wipe with acetone immediately before welding (3, 77, 78). If weld filler wire is used it must be cleaned to the same high standards as the sheet material. When possible the use of filler wire should be avoided. The cleaning procedures utilized will be discussed in Section 7.0.

Lessmann (76) reports that the porosity in GTA welded D-43 sheet could be minimized by vacuum degassing the parts after pickling and prior to welding. This indicates that either a pickling residue or adsorbed hydrogen tends to develop porosity in the welds. He reports that pickling solutions containing $\text{HNO}_3 + \text{HF} + \text{H}_2\text{SO}_4$ proved advantageous to those containing $\text{HNO}_3 + \text{HF} + \text{H}_2\text{O}$. This indicates that residues, whose removal is enhanced by including H_2SO_4 in the pickling solution, are at least partially responsible for the occurrence of porosity.

The best method for producing good GTA welds is in a controlled atmosphere chamber that has been evacuated and backfilled with an inert gas such as argon or helium. Again the use of the chamber limits the size of the workpiece.

GTA welding without a chamber is possible provided extra care is taken to adequately shield the weld zone, such as trailing shields and an adequate

backing flow of gas at the root of the weld. The shielding must be contained during welding and until the weld has cooled to below approximately 198°C (390°F) to prevent contamination. (66)

Electron-beam welding in a vacuum chamber is the preferred method for joining niobium and its alloys because the absolute welding pressure is in the order of 1.33×10^{-3} to 10^{-4} Pa, (10^{-5} to 10^{-6} torr) in the welding chamber, so the residual amounts of impurities in the atmosphere are extremely low. Also, this technique keeps the weld zone as small and cool as possible, and also permits the welding to be made as rapid as practical. The electron-beam technique has proven effective in achieving full weld penetration with an extremely narrow heat-affected zone. An obvious limitation of EB welding is the size limitation placed upon the parts to be welded, and the need for precise tooling for accurate tracking of the weld seam.

It is recommended (61) that all copper tooling have a hard chrome plate approximately .050 mm (0.002 inch) thick without a nickel strike to prevent copper contamination. Brittle welds can result from copper contamination.

Because of the inconvenience of cleaning filler wire before each welding run, it is advisable to avoid using filler wire whenever possible. For this reason, when welding thin gage material, the mating edges are sometimes rolled up to form a "burned-down flange," (61).

Typical welding conditions of 0.89mm (.035 inch) thick niobium alloys for GTA and EB welding reported by Mash, Bauer, and Schussler (56) are presented in Table II-15.

An example of a GTA welding procedure on C-103 as reported by Slosson (79) is as follows:

1. Cut to plate-size by shearing
2. Edges to be welded were machined to allow a "0" gap butt-joint.
3. Cleaning:
 - a. Degreased in vapor degreaser
 - b. Pickled in nitric-hydrofluoric acid - 5 minutes

TABLE II-15. TYPICAL WELDING CONDITIONS FOR .91 MM (0.036 IN.) SHEET⁽⁵⁶⁾

GAS TUNGSTEN-ARC WELDS				ELECTRON-BEAM WELDS					
ALLOY	SPEED, CM (IN.) PER MIN.	CLAMP SPACING, MM (IN.)	CURRENT, AMP (DCSP)	ARC GAP, MM (IN.)	SPEED, CM (IN.) PER MIN.	CLAMP SPACING MM (IN.)	DEFLECTION, MM (IN.)*	VOLTAGE, KV	CURRENT MILLIAMP
C-129Y	76.2 (30)	9.52 (3/8)	110	1.5 (0.06)	127 (50)	12.7 (1/2)	1.27 (0.050)	150	4.1
Cb-752	76.2 (30)	9.52 (3/8)	87	1.5 (0.06)	38.1 (15)	1.58 (1/16)	1.27 (0.050)	150	3.3
D-43	76.2 (30)	9.52 (3/8)	114	1.5 (0.06)	127 (50)	12.7 (1/2)	1.27 (0.050)	150	4.4
FS-85	38.1 (15)	9.52 (3/8)	90	1.5 (0.06)	127 (50)	4.76 (3/16)	1.27 (0.050)	150	4.4

* Beam deflection at 60 cycles parallel to weld direction.

- c. Dipped in chrome-sulphuric acid - 5 minutes to remove oxides formed during pickling.
- d. Hot water rinsed
- e. Hot air-blast dried.

Welding Procedure:

1. Plates to be welded were positioned in an aluminum fixture equipped with chrome-plated copper hold-down and back-up bars.
2. The fixture was placed in a controlled atmosphere welding chamber which was subsequently evacuated to .67 Pa (50 microns) and backfilled with .67 Pa argon gas or helium gas depending upon the gage of the material.
3. The plates were welded without preheat using the mechanized TIG process. No filler metal was added.
4. The following machine settings were developed and used:
 - a. .05 mm (.020") material
DC straight polarity - argon gas
110 amps
11 volts
Travel speed - 15.24 cm (6 inches) per minute.
 - b. 1 mm (.040") material
DC straight polarity - helium gas
110 amps
14 volts
Travel speed - 30.48 cm (12 inches) per minute

Kearns, et al ⁽⁷⁸⁾ have reported on the fabrication of a liquid metal loop made of Nb-1Zr. The welding was performed by GTA in a helium atmosphere in a vacuum purged chamber and in a gas purged plastic enclosure. The electrodes were 2% thoriated tungsten. The Nb-1Zr details and filler wire were chemically etched with a 20% HF-20% HNO₃ solution.

Franco-Ferreira and Slaughter ⁽⁸⁰⁾ conducted an investigation of the aging behavior of welds in Nb-1Zr alloy. They found that an embrittlement which appears to stem from a classical aging reaction occurred in the 815-980°C (1500-1800°F) temperature range. Postweld annealing in the 1037-1204°C (1900-2200°F)

range resulted in overaging which prevents embrittlement when the welds are heated subsequently at lower temperatures. Welds for this study were made in an atmosphere controlled chamber. It was observed that bend testing was a more reliable measure of embrittlement than either tensile or hardness testing. MDC⁽¹⁵⁴⁾ experienced similar embrittlement of EB welds in duplex annealed Cb-752 alloy as a result of thermal processing at 926°C (1700°F) during coating. A 1-hour vacuum stress relief at 1260°C (2300°F) reduced the problem.

6.2 Brazing

Brazing is another possible joining process for CTR first wall fabrication. Before brazing can be used routinely for CTR fabrication, some concerns not addressed in the survey or literature must be investigated. Some of these are the strength of the brazed joint required at elevated service temperature, the resistance of the braze alloy to corrosion or erosion by liquid metals, the effect of irradiation on the braze joint, and the development of field assembly or repair methods.

There have been considerable investigations on the development of brazing alloys for niobium and its alloys (48, 91, 95, 96, 97, 98, 99, 100, 101).

Brazing alloys for joining niobium alloy sandwich panels for hot structures have been developed. High temperature brazing systems for service temperatures of 1370°C (2500°F) have been reported by Young⁽⁹⁶⁾. Many of these were Ti base, Zr base, or V base alloys. The data reported for Nb-1Zr are presented in Table II-16.

TABLE II-16. Characteristics of Selected
Brazing Alloy for Niobium-1Zr⁽⁹⁶⁾

Base Alloy	Braze Alloy	Melting Range	
		°C	°F
Nb-1Zr	(Ti-6Fe-4Cr)	1495	2725 Sol.
		1566	2850 Liq.
	(Zr-28V-16Ti)	1149	2100 Sol.
		1204	2200 Liq.
	(Zr-30V-20Cb)	1204	2200 Sol.
		1260	2300 Liq.

The use of reactive metal alloys for brazing appears to be a possible method to minimize the problems of erosion and embrittlement associated with brazing using conventional high temperature, above 1930°C (3500°F), alloys. Smeltzer and Metcalfe⁽⁹⁷⁾ have studied the use of reactive alloys and conventional alloys on B66 alloy. Their data is presented in Table II-17.

For service to 1930°C (3500°F), Gilliland⁽⁹⁸⁾ has reported excellent wettability, flowability and joint integrity using Nb-Ta-V and Ti-Ta-V brazing alloys. A series of filler metals was studied by Fox and Gilliland⁽¹⁰²⁾ to braze niobium assemblies for reactor applications. Over 250 compositions were investigated.

Young, et al⁽⁹⁹⁾ studied alloy systems for use at service temperatures from 982-1204°C (1800-2200°F) for Nb-1Zr and up to 1371°C (2500°F) for F48 alloy. Their summary is presented in Table II-18.

Smeltzer, and Compton⁽¹⁰⁰⁾ developed a brazing process for Nb-1Zr heat receiver tubes. Vacuum brazing was accomplished with Zr-28V-16Ti-0.1Be alloy.

Brydges and Elrod⁽⁸⁶⁾ developed a method for brazing D-36 alloy antennas, consisting of induction brazing in an atmosphere of flowing argon at a negative pressure of 87.8 kPa (26 inches) Hg.

Brazing may be conducted in vacuum or inert atmosphere provided that the cleanliness of the parts and atmosphere are maintained to prevent contamination of the niobium.

6.3 Diffusion Bonding

This joining process appears to be very attractive for CTR fabrication because it alleviates the possible materials compatibility problems that may be associated with a brazed joint or typical concerns of a welded joint.

TABLE II-17. CANDIDATE BRAZING ALLOYS FOR B66 ALLOY⁽⁹⁷⁾

Braze Alloy	Type	Brazing Temperature		Diffusion Treatment	Remelt Temperature*	
		°C	°F		°C	°F
RGN-15	Reactive	1204	2200	1204°C (2200°F) 5 Hrs. (Vac.)	1688	3070
Ti-8.5Si	Conventional (Weakly Reactive)	1399	2550	1204°C (2200°F) 3 Hrs. (Vac.)	1443	2630
AS-536 (Ti-6Fe-4Cr)	Conventional	1566	2850	----	1816	3300
AS-501 (Ti-30V)	Conventional	1649	3000	----	1954	3550
B120 VCA (Ti-13V-11Cr-3Al)	Conventional	1621	2950	----	1832	3330
AS-514 (V-35Cb)	Conventional	1815/ 1871	3300/ 3400	----	----	----

*Taken as the temperature at which a T-joint specimen separates when heated at a rate of 38°C (100°F)/min. under a constant foil stress of 6.89 MPa (1,000 psi). (atmosphere: Ti-gettered argon).

TABLE II-18 SUMMARY OF MELTING POINT DETERMINATIONS⁽⁹⁹⁾

ALLOY DESIGNATION	NOMINAL COMPOSITION	BASE METAL	MELTING RANGE ACTUAL		AS CAST HARDNESS	DUCTILITY AS CAST	REMARKS
			°C	°F			
AS-502	95 Ti 5 Fe	Cb-1.0 Zr	1602 ⁽¹⁾ 1699 ⁽²⁾	2915 ⁽¹⁾ 3090 ⁽²⁾		Ductile	Approximate melting point - direct observation method
AS-604 A	80 Ti 20 Fe	Cb-1.0 Zr	<1149- 1204	<2100- 2200	499	Brittle	
AS-505	90 Ti 10 Cr	Cb-1.0 Zr	1602 1649	2915 3000		Ductile	Approximate melting point - direct observation method
AS-511	89 Zr 11 Al	Cb-1.0 Zr	1316- <1371	2400- <2500	494	Brittle	
AS-535	79 Ti 13 Fe 8 Cr	Cb-1.0 Zr	<1316- <1371	<2400- <2500	412	Slightly Ductile	
AS-537	56 Zr 28 V 16 Ti	Cb-1.0 Zr	>1149- <1204	>2100- <2200	391	Ductile	
AS-500	100 Ti	F-48	1699- 1704	3090- 3100	120-137	Ductile	
AS-501 A	70 Ti 30 V	F-48	<1632- <1677	<2970- <3050	229	Ductile	
AS-509	78 Zr 22 Cb	F-48	<1732- 1760	<3150- <3200	223	Ductile	
AS-513 A	80 V 20 Ti	F-48	<1732- 1760	<3150- 3200	231	Ductile	

- (1) Solidus
(2) Liquidus

There has not been any extensive study done on diffusion bonding of niobium, probably because of the good weldability of most niobium alloys.

The three types of diffusion bonding; yield stress controlled, diffusion controlled bonding, and creep controlled bonding are discussed in Section 6.3 of Part I of this report.

Dunning and Metcalfe⁽⁵²⁾ developed diffusion bonds in B66 alloy using Ta intermediate foil, contact pressure of 68.9 MPa (10 ksi), and a temperature of 1427°C (2600°F), for approximately 20 sec. All bonding was conducted in a vacuum atmosphere using resistance heating. The maximum shear stress in single lap shear specimens in the as-bonded condition was reported to be greater than 330 MPa (48 ksi).

Korman et al⁽¹⁰³⁾ investigated diffusion controlled bonding of niobium at temperatures less than 600°C (1112°F). Tests were conducted in a "gettered" atmosphere; induction heating was used.

Diffusion bonding of niobium has been investigated by Paprocki et al, (104, 105, 106). Unalloyed niobium was bonded at temperatures of 1148-1315°C (2100 to 2400°F), at a pressure of 68.9 MPa (10 ksi) for 3 hours. Joint strengths of 275.6 MPa (40 ksi) with 90% reduction in area were reported. Specimen surfaces were etched in a 65 HNO₃-35HF solution to remove .025 mm (0.001 inch) material before bonding.

Forge upset diffusion joining (FUDJ) of FS-85, Cb-752 and C-129Y was performed at McDonnell⁽¹⁰⁷⁾. Skins and corrugations were joined by the FUDJ welding method, a process which does not require a fusion weldment to be formed. The detail parts were chemically cleaned, put through a roll seam welding machine with one flat wheel for the skin side of the panel and a vee profile wheel matching the shape of the vee configuration. The operating parameters were selected to produce less than sufficient heat to form a cast nugget and enough pressure to forge the two surfaces into intimate contact. The product at this point is only superficially joined. A vacuum diffusion treatment at temperatures near 1648°C (3000°F) for times of approximately one hour was performed in which the joint was diffusion

bonded. Minor problems were encountered with unbonded areas. The FS-85 corrugated panel and joints are shown in Figure II-12.

6.4 Resistance Welding

Resistance seam welding could possibly be used for CTR fabrication if joint strengths are sufficient and if leak tightness problems do not result. Leak tight seam welds can be produced with little difficulty. However, in the event of a leak, repairing the leak can sometimes be more difficult than repairing a fusion weld.

Spot welding of FS-82 and F48 niobium alloys was reported by Neff, et al, (65). Cleaning with steel wool and rinsing with acetone produced better welds and less electrode sticking. Tungsten tipped electrodes also were found to lessen the sticking problem. Typical weld schedules for FS-82 are shown in Table II-19. Metallographic examination revealed that the weld nugget consisted of a recrystallized structure across the weld interface without fusion. If welding current was increased, fusion nuggets could be produced, but severe electrode sticking and cracking also occurred. A considerable effort was expended to develop procedures for spot welding F48. Although difficulty was encountered, satisfactory welds could be obtained under carefully controlled conditions. In general, a recrystallized nugget produced better properties than a fusion nugget.

The problem of electrode sticking was examined by Peck (54). His conclusions and recommendations are as follows:

- o The mechanisms contributing to electrode sticking appear to be: (a) mechanical bonding, (b) brazing when using copper electrodes, and (c) diffusion or solid state bonding. The first mechanism predominates when no melting occurs at the electrode sheet interface. A braze joint forms when welding with copper electrodes at sufficiently high current to cause melting at the electrode-sheet interface. Diffusion bonds are also formed when the electrode-sheet interface temperature is sufficient to cause recrystallization of the electrode.

- o Welding parameters, particularly current, have a pronounced affect on sticking. The sticking tendencies can be reduced but not eliminated

FIGURE II-12. FUDJ JOINING

TABLE II-19. TYPICAL FS-82A SPOT WELDING SCHEDULES (65)

Joint mm (in.)	Electrode/ El. Dia. mm (in.)	Weld Force N (Lbs.)	Weld Current Amps.	Heat Time	Cycles				Shear Strength N (Lbs.)
					Up Slope Time	Down Slope Time	Hold Time		
.25-.64 (.010-.025)	M-28 2.29 (.09)	667.5 (150)	6,100	6	2	3	60	667.5 (150)	
	M28 2.29 (.09)	667.5 (150)	6,100	3	0	0	60		
	M100 2.29 (.09)	1112.5 (250)	7,770	2	1	0	60		
.64-.64 (.025-.025)	M28 2.29 (.09)	979.0 (2200)	25,500	4	2	0	60	4005-4150 (900-1000)	
.25-.25-.64 (.010-.010-.025)	M100 2.29 (.09)	1112.5 (250)	8,800	2	1	0	60	867.8 (195)	
.25-1.18 (.010-.070)	M100 3.04 (.12)	2002.5 (450)	9,100	6	2	0	3		
1.18-1.18 (.070-.070)	M100 6.35 (.25)	979.0 (2200)	27,100	6	2	2	3	1201.5 (2700)	

by welding at a low electrode force and as low a welding current as possible and still produce a sound nugget of acceptable soundness. Weld time, i.e., time of current flow should be kept to a minimum. The same can be said of welding impulses. Single impulses of 5 cycles or less were found to produce less sticking than multiple impulses and large current flow times.

o The thermal and electrical conductivity of the electrode was found to significantly influence electrode sticking. RMWA Class 1 copper electrodes were generally less sensitive to sticking than the higher alloyed electrodes and copper impregnated type electrodes. This is attributed to the higher thermal and electrical conductivities of the Class 1 electrode.

o Variation in sheet and electrode surface finish had little influence on electrode sticking tendencies. This may be due to the severity of the sticking which overshadowed any benefit derived by roughening faying surfaces. In keeping with acceptable welding practice, the surface of the electrode should be maintained at a smoothed machined finish while the faying surfaces may be roughened. The outer sheet surfaces need not be prepared. There were indications that the presence of the as-received oxide on Cb-752 reduced electrode sticking tendencies. This affect was not significant when welding Ta-10W or TZM alloys.

o Variations in electrode contour had no observable influence on electrode sticking.

o Cryogenic cooling of the welding electrodes by using liquid nitrogen as the coolant offers a means of eliminating sticking when projecting cast nuggets in refractory alloys. This technique which has been developed and put into use by Ling-Temco-Vought Corporation ⁽¹⁹⁾ also reportedly provided an improvement in mechanical properties by virtue of finer grain sizes achieved through the use of the low temperature coolant.

o Electrode sticking can be eliminated by avoiding melting at the sheet faying surfaces and thus producing solid state or diffusion bonds. It is, however, not sufficient just to avoid nugget formation. The solid state bonding must be done under condition of weld current that do not overheat the electrode-sheet interface and thus produce a solid state bond between the work and electrodes. Such a bond at the electrode-work interface can lead to sticking and excessive electrode deterioration.

o Projection welding is a third method of producing strong welds in refractory metal without electrode sticking or electrode deterioration. Welds made in this program exhibited structure consisting of a cast nugget around the periphery of the projection and a solid state bond within the annular nugget. Projections made with existing tooling were not optimum in that they collapsed before experiencing enough heating to generate a weld nugget. However, the strengths obtained with the mixed weld structure were good; i.e., it may not be necessary to produce a fused projection weld to attain desired strength levels. The merits of using solid state projection welds are the same as conventional resistance solid state welding in regard to electrode sticking.

7.0 CLEANING

Cleanliness related to all fabrication-processes of Nb and its alloys cannot be overemphasized. If the interstitial elements of carbon, nitrogen, oxygen, or hydrogen are present during any elevated temperature operation such as welding or annealing, they will diffuse into the material and produce a loss in ductility or embrittle the alloy.

The usual method for degreasing is with vapor solvents or rubbing with solvents such as acetone. A thorough scrubbing with hot Alconox solution has been used to remove all traces of oil film ⁽⁵⁷⁾.

Chemical cleaning that would be used prior to vacuum annealing or welding consists of a pickling solution of $\text{HNO}_3 + \text{HF}$ or $\text{HNO}_3 + \text{HF} + \text{H}_2\text{SO}_4$. The mixtures of the acid solutions that have been used have varied, such as: 20 to 35 V/O HF + 0 to 13 V/O H_2SO_4 + 10 to 25 HNO_3 + Balance H_2O . Increased water decreases the rate of metal removal. After pickling, the material must be rinsed immediately with clean, deionized or distilled water and quickly dried with hot forced air to avoid staining. Thereafter, all handling should be done only with clean cloth gloves.

Several variations of the typical cleaning procedures have been used prior to welding or brazing. Brydges and Elrod ⁽⁸⁶⁾ report solvent degreasing with acetone prior to applying braze alloy during fabrication of antennas. Cleaning of the braze foil consisted of abrading with steel wool or 400 to 600 grit wet or dry paper followed by solvent degreasing by hand with acetone.

Lessmann ⁽⁷⁶⁾ reports that pickling solutions containing H_2SO_4 resulted in less porosity in GTA welded D-43 sheet.

Neff and Frank ⁽²⁵⁾ report vapor degreasing followed by liquid honing, and then pickling in a 20% HNO_3 + 20% HF + 60% H_2O solution, prior to GTA welding, FS-82 alloy.

8.0 THERMAL TREATMENTS

In order to achieve and maintain quality in niobium materials, it is very important that the surfaces be chemically clean before thermal treatments. It is common practice to etch approximately 0.25mm (0.001 inch) from each surface prior to vacuum annealing^(87, 108). This is done in order to eliminate the possibility of inward diffusion of interstitial contaminants such as C, H, O or N that may be present on the surfaces. Etchants used for niobium alloys are generally HNO_3 -HF- H_2SO_4 solutions; specific cleaning procedures were discussed in Section 7.0.

A clean high-vacuum annealing furnace should be used. The furnace should be capable of being evacuated to 1.33×10^{-3} Pa (10^{-5} torr) or lower and be maintained at a pressure not to exceed 1.33×10^{-2} Pa (10^{-4} torr) during the annealing cycle^(3, 87). The allowable leak rate specified by Stratton⁽³⁾ should not exceed a pressure rise from 1.33×10^{-3} to 6.65×10^{-3} Pa (1×10^{-5} to 5×10^{-5} torr) in 1 hour at room temperature.

The stress relief and recrystallization temperatures for niobium and the alloys of interest as reported in DMIC Report 188⁽¹⁰⁹⁾ and by Wah Chang Albany⁽⁶¹⁾ are presented in Table II-20.

TABLE II-20. Thermal Cycling Temperatures^(109, 61)

Alloy	Stress Relief Cycle	Recrystallization Cycle
Unalloyed Nb	1 hour 749°C (1380°F) 1 hour 871°C (1600°F) 10-15 min. at 927 to 982°C (1700 to 1800°F)	1 hour at 1149°C (2100°F) 1 hour at 1204°C (2200°F)
Nb-1Zr	1 hour at 899 to 982°C (1650 to 1800°F) 1 hour at 1149°C (2100°F)	1 hour at 1204 to 1232°C (2200 to 2250°F)
FS-85	1 hour at 999°C (1830°F) for sheet material	1 hour at 1316°C (2400°F) for sheet material
C-103	1 hour at 871°C (1600°F)	1 to 2 hours at 1204°C (2200°F)

A contamination indicator was used with each run of the furnace in work on the X-20 program ⁽³⁾. This indicator was a coupon of low carbon D-31 alloy sheet included with the furnace load. Metallographic examination of the coupon after the heat treatment showed the degree of contamination with oxygen.

For some applications where pickup or gettering of interstitials must be held to a minimum in the vacuum annealing, the material may be wrapped in clean tantalum, Nb or Nb-1Zr alloy foil. No metal-to-metal contact between niobium or its alloys, and any other metal in the furnace should be permitted since there is a chance of alloying the niobium material with the dissimilar metal.

When the material is properly cleaned before annealing and annealed with appropriate precautions, niobium alloys will have a uniform metallic, silvery-gray color. A smokey appearance on the surface or presence of stains indicates either improper cleaning before annealing or contamination during the anneal. It is important to minimize such contamination to avoid a loss in ductility or embrittlement of the niobium or niobium alloy ⁽⁵⁷⁾.

9.0 COATINGS

The same coating processes described previously for molybdenum are applicable to niobium, see Section 9.0 of Part I.

PART III - TANTALUM

TANTALUM OVERVIEW

The tantalum alloys selected for study were unalloyed tantalum, Ta-10W, and T-222 (Ta-10W-2.5Hf-0.012C). Information on other alloys is included from references, when required, to offer a broader base for background knowledge. These tantalum alloys were selected because they are commercially available and have proved to be the most fabricable for their strength levels.

Other tantalum base alloys have been investigated recently^(73, 111, 112, 113, 114, 115, 116, 117, 118, 119), however, they are not commercially available. ASTAR 811C (Ta-8W-1Re-1Hf-0.025C) which could be considered quasi-commercial⁽¹²²⁾ has attractive time dependent deformation properties at elevated temperature⁽¹²³⁾, however, only limited secondary fabrication background is available.

Tantalum possesses good low temperature ductility and good weldability which makes it attractive from a fabrication standpoint. As was the case with niobium alloys, the early alloying attempts were to increase the strength. The alloys now available are compromises between good fabricability and improved strengths.

Tantalum and its alloys of interest have DBTT well below room temperature when in the normally used, annealed condition. However, like niobium, the DBTT is raised considerably by interstitial contamination by carbon, oxygen, hydrogen, or nitrogen. This fact necessitates extreme cleanliness when performing any elevated temperature operation, such as welding, stress relieving, or annealing. Contamination will result in brittle behavior in a component or structure.

Most forming operations are performed at room temperature using essentially standard practices.

The following sections discuss the fabrication processes used on tantalum and its alloys. It includes the procedures found that have proved satisfactory for fabricating components. Because its density is almost twice that of niobium, tantalum has not been widely used to fabricate aerospace hardware. An example of a component fabricated by McDonnell from T-222 is a leading edge test model shown in Figure III-1.

VIEW OF MOLD LINE SURFACES

VIEW OF INTERNAL SURFACES

FIGURE III-1. SET OF LEADING EDGE COMPONENTS FOR
LEADING EDGE TEST MODEL

1.0 INSPECTION

The discussion on the inspection methods for niobium alloys also applies to the tantalum alloys. Both metals are from Group V of the periodic table and therefore are similar in their behavior with respect to their sensitivity to the interstitial elements of carbon, oxygen, hydrogen and nitrogen. The nondestructive and mechanical properties testing procedures also apply (refer to Section 1.0 of Part II).

A sample material specification for Ta-10W (Fansteel 60 metal) alloy is shown in Appendix C.

The "conventional" blanking processes are applicable to tantalum and its alloys and may be performed at room temperature.

Tantalum and its alloys can be blanked, punched and stamped at room temperature using steel dies with a 6% clearance. (13, 56, 62, 134)

Shearing is a very practical method of blanking parts from sheet stock. Shearing can be performed at room temperature on standard production shears. A sharp blade, set for a clearance of .025 to .05mm (0.001 to 0.002 inch) will produce clean cuts with no detectable delaminations or tears on the edges. (125)

Band sawing can be accomplished without backup. Jackson and Lopat (125) studied sawing of 1mm (0.040 inch) T-222. Their sawing parameters were a blade with 12.6 teeth/cm (32 teeth per inch) with a speed of 22.86m (75 surface feet) per minute in conjunction with a coolant of 30 parts water to 1 part Macco. Higher speeds reduced blade life. Coarser blades produced ragged cuts. These parameters vary from those in the Machining Data Handbook (23) shown in Table III-1.

Electrochemical machining can be used; however, these operations may require a high temperature vacuum or inert atmosphere anneal to remove hydrogen and prevent hydrogen embrittlement of the tantalum alloys. (56)

Care must be exercised during blanking and all other operations to prevent gouging or scratching of the tantalum alloys because they are relatively soft.

TABLE III-1. BAND SAWING RECOMMENDATIONS

HARDNESS BHN	CONDITION	MATERIAL THICKNESS mm (inches)	TOOTH FORM*	PITCH teeth/cm (teeth per inch)	BAND SPEED m/min (fpm)
200 to 250	Stress Relieved	<12.7 (<1/2) 12.7-25.4 (1/2-1) 25.4-76.2 (1-3) >76.2 (>3)	Precision	5.50 (14) 3.94 (10) 3.14 (8) 2.36 (6)	24.4 (80) 21.3 (70) 18.3 (60) 16.8 (55)

3.0 EDGE PREPARATION

Edge preparation or deburring may be accomplished using conventional techniques. Hand filing and vibratory radiusing are most often used. Edge grinding is possible, but because of the softness, especially in the annealed condition, tantalum alloys tend to rapidly load the grinding wheels or discs. (13, 19, 56)

4.0 MACHINING

Tantalum base alloys can be machined using essentially standard machining practices. The soft, ductile properties of tantalum strongly influence the machining of tantalum and its alloys of interest. The tough, stringy chips produced when machining tantalum will frequently pack and clog the flutes if improperly designed tools or excessive feeds are used. The use of highly positive rake angles and generous clearance angles on tools for tantalum are recommended. High speed steel or carbide tools can be used to machine tantalum and its alloys.

As is the case with most soft ductile materials, good surface finish is difficult to obtain. Sharp tools and moderate depths of cut must be used to produce a reasonable good surface finish and prevent burrs and rolled over edges. Liberal amounts of coolants should be used. (13, 16, 19, 20, 56, 62, 66)

The following sections describe recommendations for individual machining operations.

4.1 Face Milling

Face milling of refractory metal alloys is more difficult than turning. Super high speed steel cutters provide longer tool life than regular high speed steel cutters or carbide tools because of the rapid nose breakdown. The cutters must have a high positive radial rake angle and 0° axial rake angle. The feed should be approximately .25mm (0.010 inch)/tooth. Soluble oil (1:20) is recommended over high chlorinated or sulphurized oils. (19, 21, 66)

The basic face milling recommendations are presented in Table III-2 .

4.2 End Milling

Both slotting and peripheral end milling operations can be performed with standard HSS tools. Tools made from T-15 HSS allow cutting speeds to be increased 25% over M-3 HSS cutters. Cutters with adequate flute space

TABLE III-2. FACE MILLING RECOMMENDATIONS FOR TANTALUM

FEEDS AND SPEEDS

HARDNESS BHN	CONDITION	DEPTH* OF CUT mm (inches)	HIGH SPEED STEEL TOOL		
			SPEED m/min (fpm)	FEED mm/tooth (in./tooth)	TOOL MATERIAL
200 to 250	Stress Relieved	1.50 (.060)	18.3 (60)	.25 (.010)	T15, M33, M41 Thru M47
		.38 (.015)	24.4 (80)	.20 (.008)	T15, M33, M41 Thru M47

TOOL GEOMETRY

HARDNESS BHN	HIGH SPEED STEEL		THROWAWAY CARBIDE		BRAZED CARBIDE		CORNER ANGLE degrees	END CUTTING EDGE ANGLE degrees	AXIAL RELIEF ANGLE degrees	RADIAL RELIEF ANGLE degrees
	AXIAL RAKE ANGLE degrees	RADIAL RAKE ANGLE degrees	AXIAL RAKE ANGLE degrees	RADIAL RAKE ANGLE degrees	AXIAL RAKE ANGLE degrees	RADIAL RAKE ANGLE degrees				
200-250	0	20	5 to 7	0 to 5	0	0	45	5 to 10	10	10

for free chip flow, and relatively low feed rates and depth of cut prevent clogging of the cutter flutes by the tough stringy chips. Soluble oil performs better as a cutting fluid than either highly sulphurized or chlorinated oils. (19, 21, 66, 126)

The basic end milling recommendations are presented in Table III-3.

The basic side and slot milling recommendations are presented in Table III-4.

4.3 Turning

Straight turning operations may be performed using either HSS or carbide tools. For unalloyed Ta or 10W alloys, HSS tools are preferred. The tantalum chips tend to weld to the cutting edges of carbide tools and cause rapid tool wear; therefore, the usable range of cutting speeds for carbide tools is only slightly higher than those for HSS tools. Positive side rake angles (20 to 30°) must be used to obtain satisfactory tool life. Feed rates of .15 to .25mm (0.006 to 0.010 inch) provide the best tool life. Soluble oil is the preferred cutting fluid. (19, 21, 66)

The basic turning recommendations are presented in Table III-5.

4.4 Drilling

Drilling operations on tantalum alloys are strongly influenced by the continuous stringy chip produced and by the soft ductile nature of the material. The cutting speed and feed rate must be balanced for optimum drilling. Small diameter holes up to one diameter in depth can be drilled at cutting speeds of 15.2 to 18.2m (50 to 60 ft)/min with a feed rate of .05mm (0.002 inch)/rev. The cutting speed for holes greater than one diameter in depth should be reduced to 6.1 to 12.2m (20 to 40 ft)/min. The feed rate should not exceed .05mm (0.002 inch)/rev. for holes between 1.58 and 9.52mm (1/16 and 3/8 inch) diameter. The use of split point drills reduces the thrust and helps prevent the formation of burrs and extruded edges at the exit of the holes. (19, 21, 66)

TABLE III-3. END MILLING RECOMMENDATIONS FOR TANTALUM ALLOYS.

FEEDS AND SPEEDS

Peripheral

HARD- NESS BHN	CONDITION	DEPTH OF CUT mm (inches)	HIGH SPEED STEEL TOOL					
			SPEED m/min (fpm)	FEED – mm(inches) per Tooth				TOOL MTL
				CUTTER DIAMETER				
				mm (inches)				
				6.35 (1/4)	12.7 (1/2)	19.05 (3/4)	25 to 50 (1 to 2)	
200 to 250	Stress Relieved	1.27 (.050)	16.8 (55)	.050 (.002)	.050 (.002)	.075 (.003)	.100 (.004)	M2 M7
		.38 (.015)	19.8 (65)	.025 (.001)	.038 (.0015)	.050 (.002)	.063 (.0025)	M2 M7

Slotting

HARDNESS BHN	CONDITION	DEPTH* OF CUT mm (inches)	SPEED m/min (fpm)	FEED – mm(Inches) per Tooth				HSS TOOL MATERIAL except as noted
				WIDTH OF SLOT – mm(Inches)				
				6.35 (1/4)	12.7 (1/2)	19.05 (3/4)	25 to 50 (1 to 2)	
200 to 250	Stress Relieved	6.35 (.250)	9.1 (30)	—	—	.050 (.002)	.075 (.003)	M2, M7
		1.27 (.050)	10.7 (35)	.017 (.0007)	.025 (.001)	.038 (.0015)	.050 (.002)	

TOOL GEOMETRY

HARDNESS BHN	HELIX ANGLE degrees	RADIAL RAKE ANGLE degrees	END CUTTING EDGE CONCAVITY ANGLE degrees	AXIAL RELIEF ANGLE degrees	RADIAL† RELIEF ANGLE degrees
200-250	30	10	3 to 7	3 to 7	C

†Radial Relief Angles for Various Size End Mills:

Size*	3.18 (1/8)	4.76 (3/16)	6.35 (1/4)	9.52 (3/8)	12.7 (1/2)	19.05 (3/4)	25.4 (1)	38.1 (1-1/2)
C	19	19	15	13	13	12	10	8

*UNITS - mm (in.)

TABLE III-4. SIDE AND SLOT MILLING RECOMMENDATIONS (ARBOR MOUNTED CUTTERS)

SPEEDS AND FEEDS

HARDNESS BHN	CONDITION	DEPTH* OF CUT mm (inches)	HIGH SPEED STEEL TOOL		
			SPEED m/min (fpm)	FEED mm/tooth (in./tooth)	TOOL MATERIAL
200 to 250	Stress Relieved	6.35 (.250)	18.3 (60)	.100 (.004)	T15, M33, M41 Thru M47
		1.27 (.050)	22.9 (75)	.127 (.005)	T15, M33 M41 Thru M47

*Depth of cut is measured parallel to axis of cutter.

TOOL GEOMETRY

HARDNESS BHN	HIGH SPEED STEEL				CARBIDE			
	AXIAL RAKE ANGLE degrees	RADIAL RAKE ANGLE degrees	AXIAL RELIEF ANGLE degrees	RADIAL RELIEF ANGLE degrees	AXIAL RAKE ANGLE degrees	RADIAL RAKE ANGLE degrees	AXIAL RELIEF ANGLE degrees	RADIAL RELIEF ANGLE degrees
200-250	0	15 to 20	3 to 5	5 to 10	0	5 to 15	7 to 10	7 to 10

TABLE III-5. TURNING RECOMMENDATIONS FOR TANTALUM ALLOYS

FEEDS AND SPEEDS

HARDNESS BHN	CONDITION	DEPTH* OF CUT mm (inches)	HIGH SPEED STEEL TOOL			CAST ALLOY TOOL		CARBIDE TOOL			
			SPEED m/min (fpm)	FEED mm/rev (ipr)	TOOL MATERIAL	SPEED m/min (fpm)	FEED mm/rev (ipr)	SPEED - m/min (fpm)		FEED mm/rev (in./rev)	TOOL MATERIAL
								BRAZED	THROW- AWAY		
200 to 250	Stress Relieved	2.54 (.100)	15.2 (50)	.25 (.010)	M2, M3	16.8 (55)	.25 (.010)	25.9 (85)	-	.25 (.010)	C-2
		.38 (.015)	18.3 (60)	.12 (.005)	M2, M3	19.8 (65)	.12 (.005)	33.5 (110)	-	.12 (.005)	C-2

TOOL GEOMETRY NOTE: ALL RAKE AND RELIEF ANGLES ARE
MEASURED IN NORMAL DIRECTION.

HARDNESS BHN	HIGH SPEED STEEL AND CAST ALLOY TOOL					CARBIDE TOOLS						
	BACK RAKE ANGLE degrees	SIDE RAKE ANGLE degrees	END RELIEF ANGLE degrees	SIDE RELIEF ANGLE degrees	SIDE AND END CUTTING EDGE ANGLE degrees	BRAZED		THROWAWAY		END RELIEF ANGLE degrees	SIDE RELIEF ANGLE degrees	SIDE AND END CUTTING EDGE ANGLE degrees
						BACK RAKE ANGLE degrees	SIDE RAKE ANGLE degrees	BACK RAKE ANGLE degrees	SIDE RAKE ANGLE degrees			
170-290	0	20	5	5	5	0	20	-	-	5	5	15

Rupert⁽¹²⁶⁾ indicated that superior drill life and improved hole quality, as compared to conventional drills, were obtained with Radial Lip Pilot Point drills.

The basic drilling recommendations are presented in Table III-6.

4.5 Grinding

Grinding of tantalum alloys is difficult because of rapid wheel loading and wear. It is difficult to obtain a good surface finish on the work-piece. A severely loaded wheel results in a chattering condition. The wheel must be dressed often and flooded with grinding fluid. A "J" hardness aluminum oxide wheel is optimum. A 5% KNO_2 solution improves metal removal at wheel speeds of 610m (2000 ft)/min. Light down feeds, .025mm (0.001 inch)/pass; low table speeds in the order of 6.1m (20 ft)/min; and a cross feed of 635mm (0.025 inch)/pass are recommended for wheels speeds of 610m (2000 ft)/min. If a wheel of 610m (2000 ft)/min is not attainable or if KNO_2 is not used as the grinding fluid, the following parameters are recommended: wheel speed - 1220m (4000 ft)/min; table speed - 12.2m (40 ft)/min; down feed - .05 mm (0.002 inch)/pass; and cross feed - 1.27mm (0.050 inch)/pass; wheel - A46JV; and grinding fluid - highly chlorinated oil.^(19, 21, 23, 66, 127)

4.6 Chemical Milling

Procedures have been developed for metal removal by chemical milling using HNO_3 - HF solutions. The exact compositions are sometimes considered proprietary.

Micello⁽¹²⁸⁾ reported on chemical milling studies on Ta-10W alloy. The conclusions made during his study are as follows:

Ta-10W can be chem-milled in a nitric hydrofluoric acid solution without detrimental effects of material properties by maintaining the bath within the limits HF 13.0 -10N and HNO_3 6.5 -5N, etch rates of .012mm (0.5 mils) per minute can be obtained with surface finishes in the 25 RMS range.

TABLE III-6. DRILLING RECOMMENDATIONS FOR TANTALUM ALLOYS.

FEEDS AND SPEEDS

HARDNESS BHN	CONDITION	SPEED m/min (fpm)	FEED – mm (inches) per Revolution				HSS TOOL MATERIAL except as noted
			NOMINAL HOLE DIAMETER – mm (inches)				
			1.59 (1/16)	3.18 (1/8)	6.35 (1/4)	12.70 (1/2)	
200 to 250	Stress Relieved	15.2 (50)	.025 (.001)				T15, M33, M41 Thru M47
		16.8 (55)	–	.050 (.002)	.050 (.002)	.100 (.004)	

TOOL GEOMETRY

High Speed Steel Twist

HARDNESS BHN	POINT ANGLE degrees	LIP RELIEF ANGLE degrees	CHISEL EDGE ANGLE degrees	HELIX ANGLE degrees	POINT GRIND
170-290	118	7 to 10	125 to 135	24 to 32	Standard

Analysis for interstitial nitrogen, hydrogen, and oxygen revealed no excessive pickup due to chem-milling. Data were substantiated by mechanical testing and no detrimental effects were noted in the material properties.

Tensile, bend, and short-time creep tests showed no detrimental effects in material properties when chem-milling Ta-10W. Comparison of chem-milled tensile results with either base metal controls or previous data showed only marginal differences whether tested at room temperature or 982°C (1800°F) and whether coated or uncoated. All chem-milled and base metal control bend specimens successfully passed the bend test at 1T bend radius at room temperature and -196°C (-320°F) in either the coated or uncoated conditions.

Forming and electron beam welding studies on chem-milled Ta-10W revealed no adverse effects. Data were substantiated by metallurgical examination.

5.0 FORMING

Tantalum and its alloys are generally considered to have good formability. They behave much like mild steel except that they have a greater tendency to gall, seize and tear. Most forming operations are performed at room temperature with material in the fully annealed condition. For best forming results, sheets should have a uniform fine grain size (ASTM No. 5 or finer). Coarse-grain size results in failure by localized necking during severe forming treatments. Tantalum is ductile and can be formed and draw into complex shapes when properly lubricated. Tantalum and most tantalum alloys can be reduced in cross section by 75 to 90 percent before they require annealing. The tantalum alloys are generally considered easier to form than the niobium alloys. (16, 17, 26, 27, 56, 61, 69, 124, 129, 130)

Ekvall et al⁽¹¹⁶⁾ encountered cracking problems in machined and formed T-111 alloy. Cracking of machined thermocouple walls occurred while forming. It was suspected that residual surface stresses present at the completion of the machining operations (jig bore drilling and turning on a lathe) were responsible. A stress relief heat treatment of 1315°C (2400°F) for 1 hour in a vacuum of 1.33×10^{-3} Pa (10^{-5} torr) after machining and prior to bending solved the problem.

5.1 Brake Forming

Brake forming of the tantalum alloys of interest is possible with standard practices at room temperature. The bend ductility of fully recrystallized Ta-10W alloy is exemplified by its passing a 180° 1T bend at -196°C (-320°F). (61)

5.2 Jogging

Jackson and Lopatin⁽¹²⁵⁾ conducted jogging operations on T-222 and Ta-7W-3Re alloys. All work was performed at room temperature. Standard impact jogging die sets consisting of a clamping block and forming block on the head, and a clamping-forming block and control block on the bed of a punch press were used on 1mm (0.040 inch) thick T-222. The dies were slightly modified to produce acceptable joggles in .45mm (0.018 inch) material. The results of this work on T-222 is shown in Table III-7. Similar results were obtained with the Ta-7W-3Re alloy.

TABLE III-7. RESULTS OF IMPACT JOGGING TRIALS ON T-222 ANGLES

SPECIMEN	GAUGE, + MM (IN.)	JOGGLE		D/ +	D/ L	TOOLING	REMARKS
		DEPTH, D MM (IN.)	LENGTH MM (IN.)				
A55	1.0 (.040)	1.0 (.040)	6.85 (.27)	1.0	.15	Std. Joggle	Good
A56		1.0 (.040)	4.57 (.18)	1.0	.22	Blocks	Good
A53		1.8 (.072)	11.17 (.44)	1.8	.16		Good
A512			7.62 (.30)	1.8	.24		Good
A610			3.81 (.15)	1.8	.43		Slight pinch at Radius, Acceptable
A51		3.17 (.125)	24.38 (.96)	3.1	.13		Slight loss of joggle definition
A52		3.17 (.125)	11.17 (.44)	3.1	.28		Good
A54		3.04 (.120)	7.62 (.30)	3.0	.40		Formed depth less than 3.17mm (.125 in) set up depth
A611		3.17 (.125)	11.17 (.44)	3.1	.28		
A57							
A58							
A59							
4	0.45 (.018)	1.0 (.040)	7.62 (.30)	2.2	.13	Support for vertical leg. No overlay	Wrinkle in vertical leg
5			11.43 (.45)		.09	Overlay 3	Wrinkle reduced
6			7.62 (.30)		.13	Joggle block Modification to Support	Adjusted dies to improve clamping force-acceptable
7			3.81 (.15)		.27	Vertical Leg	Acceptable
8		1.83 (.072)	8.64 (.34)	4.0	.21		Acceptable
9		1.83 (.072)	7.62 (.30)	4.0	.24		Acceptable
10		0.68 (.027)	6.35 (.25)	1.5	.11		Good
12		0.68 (.027)	5.08 (.20)	1.5	.13		Crack-visible by penetrant inspection

1. All joggle specimens were formed from sheet stock to right angles with 2.5 x 2.5 cm (1.0 x 1.0 inch) legs. The BR of the 0.45 mm (0.018 inch) and 1.0 mm (0.040 inch) gauge angles were 0.81 and 2.29 mm (0.032 and 0.090 inch) respectively.
2. All joggles were produced on a Niagara 3 1/2 punch press under room temperature conditions.
3. Overlay consisted of angles made of 2.29 mm (0.090 inch) gauge mild steel and matched joggle specimens.

Photographs of joggle specimens are shown in Figure III-2. These show that little difficulty was experienced during joggling.

5.3 Dimpling

Jackson and Lopatin⁽¹²⁵⁾ conducted dimpling studies on .45 and 1mm (0.018 and 0.040 inch) thick T-222 and 1mm (0.040 inch) thick Ta-7W-3Re alloys. Dimpling was performed at room temperature using standard practice. In test runs on the T-222 on both material gages, undersized pilot holes of 3.86mm (0.152 inch) diameter and 2.49mm (0.098 inch) diameter were used in the 4.76 and 3.17mm (3/16 and 1/8 inch) fastener dimples, respectively, while a 2.49mm (0.098 inch) diameter pilot hole was also used in the 2.38mm (3/32 inch) fastener dimples. The parameters developed for dimpling of T-222 are shown in Table III-8.

5.4 Hydroforming

Rubber Forming - McDonnell^(125, 131) conducted studies on forming curved channel sections using the Guerin trapped rubber process on T-111 and T-222. Similar room temperature processes were used on both alloys. The procedure used on the T-222 will be described. During initial trials the stretch flange formed reasonably well but the compression flange developed wrinkles. These wrinkles could be removed by hand working. The hand working was eliminated by a multistage forming schedule. In the first stage a hard rubber wedge was added to the convex face of the form block to limit the initial deformation in the compression flange. As indicated in Figure III-3 the setup consisted of the modified form block surmounted by the blank which was then covered by an aluminum separator 1mm (0.040 inch) thick which, in turn, was topped by a quarter inch thick hard lead overlay. At the conclusion of the first pass in the hydropress a single large buckle appeared on the compression flange. In the second stage the partially formed blank and separator were set up on the unmodified form block and covered by a new hard lead overlay (see Figure III-3). The second operation did not fully set the compression flange and only a slight reduction occurred in the buckle. In the third stage the partially formed part was set on the unmodified form block and covered by a backup block. A steel plate with a matching curvature was set against the convexed face of the layup and an aluminum

T-222 1mm (0.040 Inch) Gauge

T-222 0.46 mm (0.018 Inch) Gauge

FIGURE III-2. JOGGLE SPECIMENS

TABLE III-8. PARAMETERS FOR ROOM TEMPERATURE DIMPLING OF RECRYSTALLIZED
T-222 SHEET FOR SEVERAL FASTENER SIZES ¹/₂

FASTENER SIZE AND TYPE	SHEET GAUGE mm (IN.)	DIMPLING PRESSURE SETTING	COINING RAM PRESSURE SETTING	POST HEIGHT ADJUSTMENT
2.38mm (3/32in.) Rivet	.45 (.018)	90	80	4
	1.0 (.040)	160	90	4
3.17mm (4/32in.) Rivet	.45 (.018)	50	90	4
	1.0 (.040)	130	92	
#10 Screw	.45 (.018)	65	110	4
	1.0 (.040)	190	110	4

¹ Data obtained from test operations on a Chicago pneumatic, Model CP-450 EA Hot dimpling machine. Heaters were disconnected and all dimpling operations were conducted at room temperature. The T-222 sheet in this study was in the recrystallized condition.

² A dwell time of 1 sec. was employed on all operations.

FIGURE III-3. MULTISTAGE FORMING OF T-222 CURVED CHANNELS

cover was placed over the top of the backup block and curved plate (see Figure III-3). Under this setup the pressure exerted by the trapped rubber on the head of the hydropress was efficiently distributed over the faces of the part. The third stage eliminated the buckle and fully set the flanges.

5.5 Spinning

Mash, et al, ⁽¹³²⁾ conducted spinnability tests on Ta-10W alloy during studies on Ta-10W clad with Hf-20 Ta. The following paragraphs describe their effort.

Spinning Equipment and Spin Mandrels - Equipment used for shear and form spinning experiments included a hydraulic power spinning lathe with tracing attachment, and a hand spinning lathe. Both machines were modified for high temperature spinning of refractory metals by adding water cooling facilities.

Form spinning mandrels were manufactured from H-21, H-13, and modified SAE 4355 tool steels. The shear spinnability mandrel was manufactured from triple-tempered H-21 tool steel. Two 50% reduction shear uniformity mandrels were produced from H-11 and H-13 tool steel. Although modified SAE 4355 tool steel was utilized successfully for form spinning preform mandrels, it was not suitable for final spinning mandrels due to low hot hardness and high surface flow. The H-21 tool steel exhibited excellent hot hardness during spinning tests up to 1204°C (2200°F).

Ellipsoidal preform mandrels were designed for form spinning to facilitate gradual disk breakdown with minimum edge cracking and surface checking. The basic breakdown angle from mandrel to mandrel measured at the intersection of the corner radius and the radius forming the ellipsoidal contour equaled 15°, with the exception of the first preform mandrel where the angle was tangent to the contact radius. The one inch corner radius at the holding diameter of the second preform mandrel was reduced in 3.17mm (1/8 inch) increments for each successive mandrel for the form spinning sequence. For

the optimum form spinning process, the cylindrical preform mandrel was tapered 9° to facilitate a quicker breakdown and slight extruding to a smaller diameter.

Shear Spinnability Testing of Ta-10W Sheet - Two shear spinnability tests to determine maximum wall reduction possible for Ta-10W were carried out using the above equipment. With the mandrel temperature at 427°C (800°F), disks 30.48cm (12 inches) in diameter by 3.17mm (1/8 inch) nominal thickness were shear spun at 399°C (750°F) using a 2.54 cm (one inch)/min. feed rate, 108 RPM, a roller contact radius of 7.94 mm (5/16 inch), and a cross slide pressure of 6.89MPa (1000 psi). Maximum reductions achieved in these spinnability tests were limited to approximately 55%. No failure occurred in either blank under these conditions, continuation to ultimate failure was not possible due to equipment limitations.

Shear Spinning Uniformity Tests of Ta-10W Sheet - In shear spinning, complete control of all machine variables is essential for production of spun parts with wall reductions within predetermined limits based on Sine Law calculations. Variables include machine deflection, spin roller and mandrel eccentricity, hydraulic tracer adjustment, spindle RPM and axial feed rates.

Seven .317 x 19.69cm (0.125 inches by 7-3/4 inches) diameter Ta-10W disks were prepared by machining and shear spun in the as-annealed condition at 343- 427°C (650- 800°F) spinning temperature on a 30° basic angle conical mandrel. The same spinning parameters were used as discussed previously for the shear spinnability tests.

Shear spinning tests were very successful, resulting in test cones with surface finish of 15 to 32 RMS. All specimens were under-reduced, that is, percent deviation from the Sine Law ranged from 0.8% to a maximum of 10.4%. Continuous application of Molykote No. 505 lubricant plus a constant feed rate considerably improved results.

Form Spinning Tests of Ta-10W Sheet - Initial form spinning breakdown of two spin disks was executed using hand spinning tools. However, hand spinning 3.17mm (.125 inch) thick sheet stock proved difficult and all further tests were carried out successfully on the hydraulic machine. The large hydraulic spinning lathe provided the necessary power and control to achieve desired contours with dimensional control and excellent surface finish.

A total of seven spinning operations were selected for these tests. All parts were spun at 371-399°C (700-750°F) maximum without intermediate stress relief. The gradual breakdown radius of the ellipsoidal performing mandrels facilitated easy reductions through all preforming steps. Work hardening became evident during the fifth spinning operations, indicating the desirability of an intermediate vacuum stress relief. Molykote #505 lubricant was used. Axial, cross slide and tailstock pressure was 6.89MPa (1000 psi). Mandrel speed was increased from 108 RPM (spin operations one through five) to 148 RPM for spin operations six and seven. Similarly, the form spin roller contact radius used for the first six operations was reduced from 2.54 cm (one inch) to 7.93mm (5/16 inch) for spin operation seven. For spin operations six and seven, the hydraulically operated spin roller was backed with a manually operated roller. This dual-roller set-up facilitated better control during the final sizing operations. Several acceptable plain nozzles were produced as a result of this work.

5.6 Drawing

For deep drawing operations, tantalum sheet must be in the annealed condition. It does not work harden as rapidly as most other metals; the draw depth can be as great as the diameter of the blank. When more than one drawing operation is to be performed, the first draw depth should be limited to about one-half the blank diameter. Aluminum bronze or beryllium copper dies are recommended, but the punch can be hardened tool steel unless slippage occurs. Sheet is easily formed by spinning into cups, tubes, cones, and other such shapes.⁽⁶²⁾

6.0 JOINING

Tantalum and its alloys can be joined by gas-tungsten-arc (GTA) or electron beam (EB) welding, diffusion bonding and brazing techniques. The requirements and limitations, if any, for each method will be discussed. The procedures used for tantalum are very similar to those of niobium because of the similarity in their material characteristics.

6.1 Fusion Welding

Considerable investigations have been performed to evaluate fusion welding of tantalum and its alloys. The weldability of tantalum and its alloys is generally superior to those of niobium. The discussion in this report will discuss only those alloys that are commercially available or nearly so.

The basic considerations necessary when welding tantalum are the same as those for niobium. See Section 6.1 of Part II of this report.

Contamination is the most probable difficulty that may be expected during fusion welding. Tantalum and its alloys react with and absorb the interstitial impurities, carbon, oxygen, hydrogen, and nitrogen at temperatures between a few hundred °C to about 815°C (1500°F). Above 815°C (1500°F) the solubility decreases and outgassing beings.⁽²⁷⁾ Since only a small amount of these impurities can produce severe embrittlement on subsequent cooling, it is mandatory that the area being welded be shielded from ambient atmosphere. Contamination can also decrease the alkali metal corrosion resistance of the alloys, which is of particular interest for CTR usage.^(72, 80) Tantalum alloys are perhaps less sensitive to contamination than are the niobium alloys.⁽⁷²⁾

by the distance between bead centers (L) to determine the maximum bead radius ($R_{Max.}$).

Case 2: If the known L/T is greater than the critical L/T , interpolate the tabulated L/T ratios and corresponding R/T values for splitting to determine the required R/T ratio. Multiply R/T by the material thickness (T) to determine the maximum bead radius ($R_{Max.}$).

The theoretical limit curves for drop hammer beading are presented in Figure II-9.

5.4 Dimpling

The forming limit tables by Wood ⁽³⁰⁾ are presented in Table II-9. The instructions for using the tables are as follows:

1. Determine bend angle (α) and hole radius (R) required.
2. Compare known bend angle (α) with the tabulated bend angle.

Case 1: If the known bend angle is tabulated, read the corresponding H/R value.

Case 2: If the known bend angle is not tabulated, interpolate the tabulated α and corresponding H/R ratios for splitting to determine the required H/R value.

3. Multiply H/R by the hole radius (R) to determine the length of dimple flange (H).

5.5 Hydroforming

Rubber Forming - A method of die forming sheet metal where rubber is normally used as the female die; principally used for flanging and shallow recessing. There are two process types, single and double action. In the single action process the forming pressure is exerted from only one direction, whereas in the double action process the pressure is applied from two directions. These are shown schematically in Figure I-19.

The rubber forming shrink flange limits ⁽³⁰⁾ are presented in Table II-10. The instructions for using the table are as follows:

1. Calculate R_D/T ratio from given dimensions.
2. Compare the known R_D/T with the tabulated critical R_D/T .

TABLE III-9. TYPICAL WELDING CONDITIONS FOR .89MM (0.035 IN.) SHEET

Alloy	Speed cm/min (in/min)	Clamp Spacing mm (in)	Current amp (DCSP)	Arc Gap mm (in)	Speed cm/min in/min	Clamp Spacing mm (in)	Deflection* mm (in)	Voltage Kv	Current Milliamp
T-111	38.1 (15)	9.5 (3/8)	115	1.52 (0.06)	38.1 (15)	12.7 (1/2)	1.27 (0.050)	150	3.8
T-222	76.2 (30)	6.4 (1/4)	190	1.52 (0.06)	38.1 (15)	12.7 (1/2)	1.27 (0.050)	150	4.5
10W-Ta	19.1 (7.5)	6.4 (1/4)	118	1.52 (0.06)	38.1 (15)	12.7 (1/2)	1.27 (0.050)	150	3.8

* Beam deflection at 60 cycles parallel to weld direction.

Postweld annealing may improve weld ductility in certain alloys and liquid metal corrosion resistance and thermal stability may be enhanced by postweld annealing. Thermal stability may also be improved by postweld annealing.⁽⁷²⁾

Corrosion test loop components for the Rankine system have been fabricated from T-111 by General Electric⁽¹¹⁵⁾ with no undo difficulties. Some instances of weld associated cracking occurred. A summary of the cracking incidents observed during the fabrication of the test loop components are summarized in Table III-10.⁽⁷⁵⁾ The majority of the cracking problems occurred during welding.

Gold and Kesterson⁽¹¹⁸⁾ studied GTA welding of 9.52mm (.375 inch) thick T-111 plates because the T-111 alloy has been sensitive to under-bead cracking. ^(75, 115, 116, 119) A modified welding procedure incorporating manual welding, low welding speeds, and 3 or less passes was developed which produced crack free welds in single "V" joints but only with hafnium free filler metals.

Franco-Ferreira and Slaughter⁽⁸⁰⁾ have also welded components for liquid metal service. Most of this referenced article deals with Nb-1Zr fabrication, but mentions that T-111 has also been used.

Rupert⁽¹²⁶⁾ GTA welded Z-frame edge members and doublers of T-222 alloy using T-222 filler wire. The welds were made without a chamber using a special trailing shield of argon to cover the weld area until it cooled to below 427°C (800°F). A tantalum back-up bar was used instead of copper. Clamping pressure in the fixture was light to allow for movement during welding and cooling. Tight fixturing which prevents movement will increase chances of weld cracking.⁽⁹¹⁾

TABLE III-10. SUMMARY OF CRACKING PROBLEMS ASSOCIATED
WITH T-111 TEST LOOPS

<u>CRACKING PROBLEM DURING -</u>	<u>PROBABLE CAUSE OR CONTRIBUTING CAUSE(S)</u>	<u>PREVENTATIVE MEASURES</u>
Cutting and forming	Possible nacent hydrogen embrittlement from coolant or binder in cutting wheel	Use bandsaw or tube cutters as appropriate. Use acceptable cutoff wheel and grind away cut surface to assure no cracks are present.
Machining and Forming	Residual stresses and possible hydrogen embrittlement	Use appropriate vacuum stress relief anneal.
EB and TIG Welding	Low strength of grain boundaries relative to matrix. Residual stresses	Design to avoid multipass welds. Use alloy overlay technique or intermediate stress relief for multipass welds when necessary. Use EB welding as much as possible. Stay on low Hf side of specification and use double arc melted alloy. Stress relieve machined parts before welding. Provide adequate mechanical support for welding.
Spot tack welding	Cu High Hf concentration in grain boundaries.	Avoid use of Cu electrode; use Mo electrode.

Jackson and Lopatin⁽¹²⁵⁾ conducted a program on structural use of tantalum alloys which included electron beam welding. They report that T-222 alloy retained its good ductility after welding, while welding reduced the ductility in Ta-7W-3Re and Ta-10W-2.5Mo alloys. The ductility of the latter two alloys could be restored by a postweld heat treatment for one hour at 1315°C (2400°F) in a vacuum.

Baker⁽¹³⁷⁾ reported an electron beam welded dissimilar metal joint between a tantalum T-222 flame liner and a niobium C-103 reservoir jacket. Square butt joints in 3.3 mm (0.130 inch) thick sheets were welded using a 60 Kv EB welding unit and the following schedule:

Beam Current	150 ma
Voltage	25 Kv
Focus Current	4.4 amperes
Filament Current	52 amperes
Speed	127 cm/min (50 ipm)
Gun-to-Work Distance	5.08 cm (2 inches)

The welds had a minimum bend radius of 4T at room temperature. The welding of the dissimilar metals did decrease the weld ductility from 2T at -196°C (-320°F).

The following is a list of articles and reports concerned with welding of tantalum: (13, 16, 17, 26, 27, 40, 56, 62, 69, 71, 72, 73, 74, 75, 76, 80, 81, 84, 91, 116, 124, 126, 129, 133, 134, 138, 139, 140).

6.2 Brazing

There has not been a great deal of investigation into the brazing process for tantalum and its alloys, primarily because of the excellent weldability of tantalum. Brazing could be considered as an alternative joining process.

Brazing has been accomplished in both vacuum and argon atmospheres. The braze alloys used for conventional brazing of tantalum alloys reported by Mash, et al⁽⁵⁶⁾ are shown in Table III-11.

Braze alloys proposed for diffusion sink brazing of Ta-10W are shown in Table III-12⁽²⁶⁾. The diffusion sink technique uses a braze alloy with a relatively low melting point that reacts with a powder and/or refractory metal during the braze cycle to form a new alloy in the joint that has a higher melting point.

Freedman et al^(47, 49) conducted brazing studies on tantalum honeycomb structures applicable for service temperatures of 1927°C (3500°F). For conventional brazing the braze alloy was Hf-40Ta. For diffusion sink brazing the braze alloy was Hf with 7 to 10 percent Mo.

Rupert⁽¹²⁶⁾ conducted brazing tests on T-222 honeycomb structures. The brazing alloy Hf-19Ta-2.5Mo powder resulted in satisfactory filleting at temperatures of 2116 to 2260°C (3840 to 4100°F), however, the braze joint was brittle. A process using Nb-65V foil braze alloy was effective and reliable. The brazing was conducted in a vacuum of 1.33×10^{-2} to 1.33×10^{-3} Pa (10^{-4} to 10^{-5} torr).

Cleanliness was the factor mentioned throughout the literature as being extremely important for producing brazed joints that are good quality.

6.3 Diffusion Bonding

Diffusion bonding appears attractive for CTR fabrication because it alleviates some possible material compatibility problems that may be associated with brazed joints or the typical concerns of a welded joint.

There has not been extensive study on diffusion bonding of tantalum, probably because of the good weldability of the tantalum alloys.

The types of diffusion bonds and the factors which affect diffusion bonding were described in the niobium section (see Section 6.3 of Part II).

TABLE III-11. TYPICAL BRAZING FILLER METALS AND SERVICE TEMPERATURE (56)

FILLER METALS	MAXIMUM SERVICE TEMPERATURE	
	°C	°F
For Tantalum Alloys:		
7Mo-Hf	2,093	3,800
20Cb-20Ta-60V	1,871	3,400
15Ta-25V-60Ti	1,649	3,000
10Hf-(15-70)Cb-Ta	2,204	4,000
(30-50) Hf-Cb	2,204	4,000
10Hf-Ta	2,204	4,000
1.38-Cb	1,927	3,500
Copper	982	1,800

TABLE III-12. PROPOSED DIFFUSION SINK BRAZE ALLOYS (21)

Braze Alloy							Melting Point	Addition (powder)	Remelt Temperature
Zr	Ti	V	Fe	Si	Mo	Ta			
							°C	°F	
43	25	32					1221	2230	Mo or Nb + C or B
	66	27	7				1482	2700	Ta
	69	29		2			1549	2820	Ta or Mo
28	47				15	10	1649	3000	Ta
	52	21.5		1.5		25	1660	3020	Mo
									1871°C (3400°F)

Korman et al⁽¹⁰³⁾ investigated diffusion controlled bonding of tantalum at temperatures less than 599°C (1112°F). Tests were conducted in a "gettered argon" atmosphere; induction heating was used.

Solid state bonding of tantalum honeycomb core was reported by Hugill and Gainnie.^(141, 142)

Dunning and Metcalfe⁽⁵²⁾ developed yield stress controlled diffusion bonds in Ta-10W alloy using tantalum and niobium intermediate foils, contact pressure of 689 MPa (10 ksi), a temperature of 1428°C (2600°F) for approximately 20 seconds. All bonding was conducted in a vacuum atmosphere using resistance heating. The procedure for preparation of the surfaces for diffusion bonding are shown in Table III-13.

TABLE III-13. PREPARATION OF 90 TANTALUM-10 TUNGSTEN ALLOY FOR DIFFUSION BONDING⁽⁵²⁾

PROCEDURE	COMMENTS
Abrade with 3/0 emery paper	Perpendicular to length of bond
Degrease in constant temperature Pennsalt 45 solution	3 to 4 minutes at 93°C (200°F)
Rinse in distilled water	Room temperature
Immerse in tantalum etch for 2 to 4 seconds at room temperature	4 parts H ₂ SO ₄ concentrated 1 part HF concentrated Alloy should etch bright
Wash in distilled water	Room temperature
Dry with bottled dry nitrogen	Blast nozzle used

6.4 Resistance Welding

There was no available data that provided information on resistance welding of tantalum and its alloys.

Because of the similarity between tantalum and niobium, one would surmise that the resistance welding characteristics would be similar. Naturally more heat would be required to develop a weld nugget in the high melting point tantalum alloys.

Electrode sticking is a problem encountered in resistance welding of refractory metals and would probably exist for tantalum. The results of an investigation to determine the causes of electrode sticking conducted by Peck⁽⁵⁴⁾ were discussed previously in Parts I and II of this report.

7.0 CLEANING

Cleanliness is important to all elevated temperature processing of tantalum and its alloys. If the interstitial elements of carbon, nitrogen, oxygen, or hydrogen are present during any elevated temperature operation such as welding or annealing, they will diffuse into the material and produce a loss in ductility or raise the DBTT.

The usual method for degreasing is with vapor solvents or rubbing with solvents such as acetone.

Chemical cleaning that would be used prior to vacuum annealing or welding consists of a pickling solution of $\text{HNO}_3 + \text{HF}$ or $\text{HNO}_3 + \text{HF} + \text{H}_2\text{SO}_4$. The mixtures of the acid solutions that have been used have varied, such as: 20 to 35 V/O HF + 0 to 13 V/O H_2SO_4 + 10 to 25 HNO_3 + Balance H_2O . Increased water decreases the rate of metal removal. After pickling, the material must be rinsed immediately with clean, deionized or distilled water and quickly dried with hot forced air to avoid staining. Thereafter, all handling should be done only with clean cloth gloves. (16, 26, 126, 143)

Examples of specific cleaning procedures that have been used are given below.

The cleaning procedure reported by Kammer et al. ⁽¹³⁴⁾ for cleaning tantalum alloys prior to GTA welding are as follows: a) rinse in acetone, b) pickle for 30 seconds in a mixture of 55 percent H_2SO_4 + 25 percent HNO_3 + 20 percent HF, c) rinse in warm water, and d) dry with a warm air blast.

Dunning, et al ⁽⁵²⁾ used the cleaning procedure shown in Table III-13 to prepare Ta-10W alloy surfaces for diffusion bonding.

8.0 THERMAL TREATMENTS

In order to achieve and maintain quality in tantalum materials, it is necessary that the surfaces be chemically clean before thermal treatments. It is common practice to etch approximately .025 mm (0.001 inch) from each surface prior to vacuum annealing. This is done to eliminate the possibility of inward diffusion of interstitial contaminants such as C, O, H or N that may be present on the surface. Etchants used for tantalum and niobium are generally $\text{HNO}_3 + \text{HF} + \text{H}_2\text{SO}_4$ solutions; specific cleaning procedures were discussed in Section 7.0.

A clean high vacuum annealing furnace should be used. The furnace should be capable of being evacuated to 1.33×10^{-3} Pa (10^{-5} torr) or lower and be maintained at a pressure not to exceed 1.33×10^{-2} Pa (10^{-4} torr) during the annealing cycle.^(61, 73, 87, 126, 143, 144)

Unalloyed tantalum or Nb-1Zr alloy foil is sometimes wrapped around parts to be thermally cycled to protect the parts from contamination.

A 1 hour, 1316°C (2400°F) post weld anneal to T-111 and T-222 alloys has been recommended by Lessmann⁽⁷⁶⁾.

The stress relief and recrystallization temperatures for tantalum and its alloys of interest as reported in DMIC Report 189⁽¹²⁴⁾ and NASA CR-121096⁽¹¹⁷⁾ are presented in Table III-14.

TABLE III-14. THERMAL CYCLING TEMPERATURES

<u>Alloy</u>	<u>Stress Relief Cycle</u>	<u>Recrystallization Cycle</u>
Unalloyed Ta	1 Hr. at 982°C (1800°F)	1 Hr. 1199 to 1399°C (2190 to 2550°F) $\triangle$
T-222	1 Hr. at 1204°C (2000°F) 2	1 Hr. at 1649°C (3000°F) $\triangle$
Ta-10W	1 to 3 Hrs. at 1093 to 1232°C (2000 to 2250°F)	1 Hr. at 1316 to 1482°C (2400 to 2700°F)
ASTAR-811C		1/2 Hr. at 1982°C (3600°F)

$\triangle$ Cold reduced 50 and 75 percent from as-cast ingot, respectively

$\triangle$ Reduced 90 percent.

9.0 COATINGS

The same coating processes described previously for molybdenum are applicable to tantalum, see Section 9.0 of Part I.

PART IV - VANADIUM
VANADIUM OVERVIEW

Vanadium and the vanadium alloys are very specialized materials and were developed almost exclusively for the Atomic Energy Commission. Very little information relating to fabrication methods was found for vanadium and what little information was available was included in alloy development or material evaluation studies.⁽¹⁴⁵⁻¹⁵⁹⁾

Vanadium alloys can be strengthened by both solid solution alloying with other metals, including most refractory metals, and by dispersion strengthening with small amounts of carbon. Nominal compositions of some alloys included in development programs sponsored by the Atomic Energy Commission are listed in Table IV-1.^(145,159)

TABLE IV-1. NOMINAL COMPOSITIONS (WT %) OF
CANDIDATE FUEL-CLADDING ALLOYS^(145,159)

<u>V</u>	<u>Ti</u>	<u>Cr</u>	<u>Fe</u>	<u>Ta</u>	<u>Nb</u>	<u>Zr</u>	<u>C</u>
80	20						
78.5	15	7.5					
80	5	15					
90		10					
86.5		9	3			1.3	0.05
80.5		8		10		1.3	0.05
87.5			6		5	1.3	0.05
80					20		

Vanadium forms an oxide, V_2O_5 , that melts at 677°C (1250°F), therefore, vanadium and its alloys must be protected from exposure to oxidizing atmospheres at elevated temperature.^(146,155) The V_2O_5 is toxic and a health hazard exists if fine swarf ignites during machining.

Vanadium has a ductile to brittle transformation temperature of -60 to -206°C (-76 to -338°F), dependent upon the oxygen, nitrogen, and carbon content.⁽¹⁴⁷⁾ Therefore, most forming operations can be conducted at room temperature.

The following sections describe the fabrication processes for vanadium and its alloys.

1.0 INSPECTION

The discussion on the inspection methods for niobium alloys will also apply to the vanadium alloys. Both metals are Group V metals and therefore are similar in their behavior with respect to the interstitial elements.⁽¹⁵⁵⁾ The nondestructive and mechanical properties testing procedures also apply. Refer to Section 1.0 of Part II.

2.0 BLANKING

The "conventional" blanking procedures including shearing or band sawing should be applicable to vanadium and its alloys and may be performed at room temperature. Whitlow et al⁽¹⁵⁸⁾ sheared 0.81 mm (.032 in.) sheet at room temperature. Very little information was revealed that pertained to blanking processes, which may indicate that no difficulties have been encountered in the past. Vanadium and its alloys have a tendency to gall, therefore, sawing procedures should be adjusted accordingly.

3.0 EDGE PREPARATION

Edge preparation or deburring may be accomplished using conventional techniques. Royster et al⁽¹⁴⁸⁾ reported satisfactory edge preparation for coating test specimens by tumbling in a ball mill using a dry mixture of pebbles and 180 grit silicon carbide for approximately 150 hours to produce rounded edges and corners. This method is very slow and applicable only to very small parts.

4.0 MACHINING

Unalloyed vanadium is free-cutting. Good results have been obtained with tool characteristics similar to those used for machining copper. Alloyed vanadium alloys are more difficult to machine.^(147, 149)

Pigott⁽¹⁴⁶⁾ reports that V_2O_5 is toxic and a health hazard exists if fine swarf ignites during machining. The fire hazard can be eliminated by using coolants although this complicates the swarf recovery process.

For swarf recovery reasons vanadium and its alloys may be machined "dry;" the rate of metal removal is limited by the ignition characteristics of the swarf. ⁽¹⁴⁶⁾ Rostaker ⁽¹⁴⁹⁾ reports that a light lubricant such as kerosene, combined with high cutting speeds, and a light cut are recommended for a good surface.

High speed steel tools have a fair life despite serious "pick-up" of metal during machining. Tungsten carbide tipped tools have an improved life but metal adherence is similar. ⁽¹⁴⁶⁾

4.1 Turning

A turning speed of about 18.3 m/min (60 ft/min) with a feed of 0.25 mm/rev (0.01 in./rev) on a one inch diameter stock using a tool with a 20° top rake is reported to give good results. Light cuts should be avoided. ⁽¹⁴⁶⁾

4.2 Milling

High speed steel cutters have been used dry at a variety of speeds which were set by the ignition characteristics of the swarf. ⁽¹⁴⁶⁾

V-20Nb has been machined at a cutting speed of 100 revolutions per minute, table feed of 19 mm (0.75 inch) per minute and a depth of cut of 0.38 mm 0.015 inch with no difficulty. ⁽¹⁴⁸⁾

4.3 Drilling

Dry drilling with high speed steel 118° point angle drills is affected by the galling tendencies of vanadium and its alloys. ⁽¹⁴⁶⁾

5.0 FORMING

Vanadium and its alloys should have good formability, although very few reports discuss formability or describe forming processes that have been used.

Unalloyed vanadium does not work harden rapidly and may be cold worked readily ^(147, 149, 157)

Royster, et al⁽¹⁴⁸⁾ reports that forming operations can be accomplished with relative ease on the V-20Nb alloy.

Bill⁽¹⁵⁰⁾ reports that curved channels were formed in V-20Nb-4Ti-1Zr-0.07C alloy using hard and soft lead overlays in a process similar to that used by McDonnell^(125, 131) to form T-111. No signs of cracking were observed. See Section 6.4 of Part III for forming procedures.

Bend tests on a V-20Nb-4Ti-1Zr-0.07C alloy indicated that 1T bends could be formed at room temperature.⁽¹⁵⁰⁾

Drawing of unalloyed vanadium has been used to form tubes with dimensions of 1.57 mm (0.062 inch) I.D. x 0.25 mm (0.010 inch) wall, which represented a total reduction from the original extruded tube of 98%.⁽¹⁴⁹⁾ Burt, et al^(151,156) report that V-20Ti (TV-20) alloy exhibited fabricability during tube drawing similar to that of D-43 niobium alloy, but showed a tendency to gall during drawing through carbide dies.

6.0 JOINING

Vanadium and its alloys can be joined by gas-tungsten-arc (GTA) or electron beam (EB) welding or resistance welding. One would expect that since vanadium, niobium and tantalum are all Group V metals, they would react similarly during welding.

6.1 Fusion Welding

More information has been published on welding than the other phases of secondary fabrication.

Welding requires protective atmospheres to prevent reaction with oxygen and nitrogen at temperatures above approximately 300°C (575°F).⁽¹⁴⁷⁾

Royster et al⁽¹⁴⁸⁾ conducted welding studies on V-20Nb and a Nb-40V alloys. The parameters were determined through experimentation on small specimens. Table IV-2 contains the parameters for both GTA and EB welds. To evaluate the welds, bend tests were conducted with the weld perpendicular

TABLE IV-2. PARAMETERS FOR THE BUTT
WELDING OF VANADIUM ALLOYS⁽¹⁴⁸⁾

(a) Tungsten Inert Gas		(b) Electron beam	
Machine type	- ac, dc inert arc and metal arc welder	Accelerating potential	- 120 kV
Flow rate	- Argon	Beam current	- 2.8 mA
Torch type	- Heliarc	Welding speed	- 50.8, 76.2, and 101.6 cm/min (20, 30, and 40 in./min)
Torch size	- M 50A	Beam deflection	- 0
Electrode	- 2.38 mm (3/32 inch) thoriated tungsten	Vacuum	- 1.33×10^{-2} Pa (10^{-4} mm Hg)
Shielding gas	- Argon		
Flow rate	- $0.57 \text{ m}^3/\text{hr}$ (20 cu ft/hr)		
Travel speed	- 88.9 cm/min (35 in./min)		
Polarity	- Direct current, straight polarity		
Current	- 120A		

to the contact radius of the ram during testing. The results are shown in Table IV-3. Good welds were produced in both alloys without embrittlement using GTA or EB welding techniques. The alloys exhibited good bend ductility; however, the V-20Nb did show some slight cracking.

Rajala, et al⁽¹⁵⁷⁾ made a cursory study on welding V-5Ti-20Nb alloy by GTA welding 1.25 mm (.050 in.) sheet with He as the protective atmosphere. Tensile test specimens failed in the heat affected zone or the parent metal, and no serious degradation was noted.

Bill⁽¹⁵⁰⁾ reports good weldability of V-20Nb-4Ti-1Zr-0.07C alloy using GTA. Tensile tests of GTA welds showed yield and ultimate strengths equivalent to base metal properties, F_{ty} - 541 MPa (78.5 ksi); F_{tu} - 698 MPa (101.3 ksi). An 8T bend radius was successfully formed on a welded specimen with the weld perpendicular to the bend axis. A crack developed in the weld and heat affected zone when a 4T radius was attempted.

Kramer, et al⁽¹⁵²⁾ report welding studies on a V-15Ti-7.5Cr alloy. They indicate a high degree of weldability with both GTA or EB welding. They felt that the alloy showed a more controllable fusion zone than 304 stainless steel. GTA welds were used to seal end plugs onto tubes. EB welding was conducted on a 1.5 mm (0.060 inch) sheet of the alloy. Tensile tests on EB welded specimens with single pass, full penetration or two passes (one per side) indicated only slight loss in strength as compared with base metal properties. The fractures were ductile and well away from the weld and heat affected zones. Slight porosity was evident in metallographic analysis. In general, they felt that the welds were excellent considering that no attempts were made to optimize the welding parameters.

Pollack, et al⁽¹⁵⁹⁾ report that satisfactory welds could be achieved in most of the experimental alloys that they were investigating; however, post annealing was required to depress the DBTT of the weldments to below room temperature.

TABLE IV-3. BEND TEST DATA FOR WELDED
UNCOATED V-Nb SHEET

Material	Type of Weld	Weld Speed cm/min (in./min)	Ultimate Load N (lb)	Bend angle at Ultimate Load, Deg	Load at Failure N (lb)	Bend angle at Failure Deg
V-60Nb	Tungsten Inert Gas		2936 (660)	20	(*)	(*)
V-20Nb	Tungsten Inert Gas		1810 (407)	22	1214 (273)	40
V-20Nb	Electron Beam	101.6 (40)	1868 (420)	22.5	(*)	(*)
V-20Nb	Electron Beam	76.2 (30)	1868 (420)	22.5	(*)	(*)
V-20Nb	Electron Beam	50.8 (20)	1868 (420)	22.5	(*)	(*)

*Specimen did not fail.

6.2 Resistance Welding

Bill⁽¹⁵⁰⁾ reports resistance welding studies on V-20Nb-4Ti-1Zr-0.07C alloy. The resistance welding parameters are shown in Table IV-4. The spot welded lap shear average strength was 11,920N (2680 pounds) and tensile pull-out average strength was 4226N (950 pounds). The tests were conducted on 1.25 mm (0.050 inch) thick sheet material.

7.0 CLEANING

Cleanliness related to fabrication processes is important for any elevated temperature process. If the elements of nitrogen or oxygen are dissolved into the metal it will cause embrittlement.

Vanadium can be chemically cleaned by pickling in a solution of 30% HNO_3 and 3% HF in water. Pickling can produce hydrogen embrittlement in the metal, which can be removed by vacuum annealing at 1000°C.⁽¹⁴⁹⁾

8.0 THERMAL TREATMENTS

It is necessary that the surfaces be chemically clean prior to thermal treatments to avoid embrittlement from oxygen or nitrogen. Cleaning can be accomplished in a 30% HNO_3 + 3 HF + balance water solution.

Vanadium reacts actively with air, CO, CO_2 and hydrocarbon gases at elevated temperatures. Annealing temperatures are generally above the melting point of V_2O_5 . Accordingly, vanadium should be annealed in a neutral, helium or argon atmosphere or in a vacuum.⁽¹⁴⁹⁾

Recrystallization of unalloyed vanadium occurs at approximately 750°C (1380°F) after 1 hr⁽¹⁴⁷⁾; the exact temperature is dependent upon the amount of cold work in the material.

Burt, et al^(151,156) reports annealing V-20Ti alloy at 900-950°C (1650-1740°F).

TABLE IV-4. SPOTWELDER QUALIFICATION DATA

SERIAL NO.: 51170		MAKE: TAYLOR WINFIELD	DATE: 12/10/63	KVA: 100
ELECTRODE CONTOUR AND SIZE: MALLORY-3		WELD TIME:	185	
MINIMUM CONTOUR DIA.: 12.7 mm (1/2 in.)		POST HEAT TIME	100	
		TOTAL WELD TIME	285	
		FORGE DELAY TIME	OFF	
		HOLD TIME	1501	
UPPER	10R	OFF TIME	334	
MINIMUM CONTACT DIA.		PRESSURE: 1/2	AIR PRESSURE 40	
			FINAL ELECTRODE FORCE 2800	
			SINGLE OR DOUBLE	
			PRESSURE (SINGLE) HIGH	
LOWER	10R			
ELECTRODE MATERIAL		ELKALAY		
DISTANCE BETWEEN		8		
THROAT DEPTH		38		
H	TRANSFORMER TAP SETTING	WYE	HIGH	
E	TRANSFORMER SWITCH SETTING	7	7	
A	POST HEAT DIAL SETTING		80	
T				

MATERIAL COMBINATION: 1.25 mm to 1.25 mm (.050 in. to .050 in.), VANADIUM

The optimum annealing temperature for cold worked stock of V-Nb-Ta alloys with small additions of Ti, Si, and C was reported in the 1200-1260°C (2200-2300°F) range.⁽¹⁵³⁾

9.0 COATING

The same coating processes described previously for molybdenum are applicable to vanadium; see Section 9.0 Part I.

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APPENDIX A

STANDARD MATERIAL SPECIFICATION FOR MOLYBDENUM
ALLOY STRIP, SHEET AND PLATE (Mo - 0.5Ti - 0.07 Zr)
MCDONNELL DOUGLAS CORP.

MMS-184

MOLYBDENUM ALLOY STRIP, SHEET & PLATE

(MOLYBDENUM-0.5% TITANIUM-0.07% ZIRCONIUM)

1.0 SCOPE

- 1.1 This specification establishes the requirements for chemical and mechanical properties of one type of molybdenum alloy intended for use in the fabrication of airframe components where strength at temperatures above 1800°F is required.
- 1.2 This material is not recommended for use in oxidizing atmospheres at 800°F or above unless protected by a suitable coating.

2.0 APPLICABLE DOCUMENTS

- 2.1 The following applicable documents, of the issue in effect on the date of invitation for bids, form a part of this specification to the extent specified herein.

Standard, Federal

Federal Test Method Standard No. 151 - Metal, Test Methods.

- 2.2 OTHER PUBLICATIONS: The following documents form a part of this specification. Unless otherwise specified, the issue in effect on the date of invitation to bid shall apply.

Aeronautical Material Specification

AMS-2242 - Tolerances - Corrosion and Heat Resistant, Sheet, Strip, and Plate, except as noted in Paragraph 3.71.

3.0 REQUIREMENTS

- 3.1 MATERIAL AND WORKMANSHIP: Material shall be vacuum arc melted using consumable electrode practice. The product shall be uniform in quality and condition, clean, sound, smooth and free of foreign materials and from internal and external imperfections detrimental to the fabrication or to the performance of parts. The material shall be free of any deleterious contaminated surface. A hardness traverse shall show less than 50 Vickers Hardness Number variation across the thickness of the material.

- 3.2 CONDITION: Unless otherwise specified, material shall be hot-cold worked, stress relieved in hydrogen or vacuum at a minimum temperature of 2100°F for one hour and pickled. The material shall have a matte surface appearance as close as possible to a commercial corrosion resistant steel No. 2D finish. Standard for acceptance and rejection shall be as agreed upon by purchaser and vendor. Surface defects may be removed providing the conditioning does not exceed the thickness tolerance.

- 3.3 CHEMICAL COMPOSITION: The chemical composition of the material in percent by weight shall be as follows:

ELEMENT	CHEMISTRY	CHECK ANALYSIS
Oxygen	0.0025 max. (1)	
Nitrogen	0.002 max. (1)	
Hydrogen	0.001 max. (1)	
Carbon	0.01 to 0.03	+0.005
Iron	0.010 max.	+0.002
Nickel	0.005 max.	+0.001
Silicon	0.010 max.	+0.002
Titanium	0.40 to 0.55	±0.05
Zirconium	0.06 to 0.12	-0.02
Molybdenum	Balance	

3.3 (Continued)

- (1) Deviation from these limits alone shall not be cause for rejection if all other requirements of this specification are fulfilled.

3.4 MECHANICAL PROPERTY - For all tensile tests, a strain rate of 0.005 inch/inch/minute through the 0.2% yield strength and 0.02 inch/inch/minute thereafter shall be used.

3.41 Room Temperature Tensile Properties: The tensile properties of the material as supplied, at a temperature of 750 ± 100°F, and transverse to the direction of final rolling shall conform to the requirements specified in Table I.

3.42 Elevated Temperature Tensile Properties: Table II specifies the minimum tensile properties of the material as supplied when tested transverse to the direction of final rolling at the test temperature for 30 minutes prior to testing. Only one elevated temperature between 1800°F and 2400°F should be specified for procurement purposes.

3.5 BEND TRANSITION TEMPERATURE TEST FOR SHEET AND STRIP

3.51 Test specimens shall be strips 1.0 inch wide and at least 2 inches long cut transverse to the final rolling direction. Edges shall be free of stress risers.

3.52 The bend transition temperature shall not exceed 32°F. Defined as the minimum temperature at which a specimen 0.060 inches or less in thickness may be bent through a 105° angle over a 2T radius using a ram speed not less than 10 inches per minute. (T = sheet thickness).

3.6 RECRYSTALLIZATION

3.61 Not more than 5% recrystallized grains shall be observed metallographically after heating previously stress relieved material for one hour at 2200°F. Figure 1 shall be used as a reference standard for estimating percent recrystallization.

3.62 Specimens of sheet when deliberately recrystallized between 70 and 90% shall generally have a uniform grain size across the thickness of the sheet. Lack of recrystallization or fine grain size adjacent to the surface is indicative of contamination and shall be cause for rejection.

3.7 TOLERANCES: Unless otherwise specified, tolerances shown herein shall apply.

3.71 Thickness

Nominal Thickness Inches	Thickness Tolerance, Inches Plus or Minus Width Ranges, Inches			
	14 & Under	12-24	24-30	30-48
0.011 and under	-	*	-	-
0.012 to 0.019	.0015	*	-	-
0.020 to 0.029	.002	*	-	-
0.030 to 0.039	.0025	*	-	-
0.040 to 0.049	.003	*	-	-
0.050 to 0.090	7.5%	*	-	-
Over 0.100	10%	*	-	-

* AMS 2242, Table II

ISSUED 10 July 1961 REVISION C 23 January 1961	MOLYBDENUM ALLOY STRIP, SHEET AND PLATE (MOLYBDENUM - 0.5% TITANIUM - 0.07% ZIRCONIUM)	MMS- 184
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3.72 Width, Sheared Flat Sheet and Plate

Width Tolerance, Inch
Plus or Minus

Under .1875 1/16
.1875 and Over 1/8

3.73 Length, Sheared Flat Sheet and Plate

Length Tolerance, Inch
Plus or Minus

Under .1875 3/32
.1875 and Over 1/8

3.74 Camber, Sheared Flat Sheet

Camber Tolerance, Inch
Plus or Minus

Nominal Length, Inches

95 Inches and Under 3/32

3.75 FLATNESS - Flatness tolerance will not exceed 5% for gages 0.010 and 0.017 and 4% for gages over 0.017.

$$\% \text{ Flatness} = \frac{H}{L} \times 100$$

Where: H is equal to the maximum distance between a flat surface and lower surface of sheet and L is equal to the minimum distance between points of contact of the sheet with a flat surface.

If a general bow in the material can be eliminated by slight pressure without ends coiling or an oil can effect resulting, the material will be accepted.

3.8 IDENTIFICATION: Unless otherwise specified, each form of material shall be marked in characters not less than 3/8 inch in height with suitable marking fluid having no deleterious effect upon the material. Markings shall be spaced not more than 12 inches apart with alternate rows staggered. The markings shall not rub or smear off in normal handling and shall be capable of being removed by a cleaning solution without rubbing. Markings shall be as follows:

Manufacturer's name or identification
Manufacturer's alloy designation
Manufacturer's heat number
MMS-184
Nominal Thickness

4.0 QUALITY ASSURANCE PROVISIONS

4.1 Test coupons shall not be removed from the final product for material qualification tests unless specified on the purchase order for the material. When testing is specified, test coupons shall be removed from only one sheet of each gage from each heat of material in the shipment unless otherwise specified.

4.11 Each sheet of material received shall be fully inspected to determine compliance with the requirements of Paragraphs 3.1 (Workmanship), 3.6 (Recrystallization), 3.7 (Tolerances) and 3.75 (Flatness).

4.12 Inspection Performance: - When authorized on the purchase order, compliance with this specification shall be checked by the MAC Quality Assurance Department. Only those tests specified on the purchase order shall be accomplished. No other destructive tests shall be initiated without specific written approval of the Project Strength Engineer. A copy of the results of all tests shall be forwarded to the Metallurgical Group, Material and Process Development Department, and the Project Strength Engineer responsible for the project procuring the material.

4.2 SAMPLING, INSPECTION AND TESTS: Sampling, inspection and tests shall be in accordance with Federal Test Method Standard 151.

4.3 VENDOR REPORTS: Unless otherwise specified, the Vendor of the product shall furnish with each shipment three (3) copies of a report of the results of tests on each thickness or size from each heat. The report shall include results of chemical analysis, room temperature and one elevated temperature tensile, recrystallization and bend tests as well as purchase order number, heat number, material specification number, thickness, size and quantity from each heat. One copy of the test report furnished by the Vendor shall be forwarded to the Metallurgical Group, Material and Process Development Department. One copy of the test report furnished by the Vendor shall also be forwarded to the Project Strength Engineer responsible for the project procuring the material.

NOTE: Elevated temperature tensile specimens shall be free of contamination after test.

4.4 REJECTION: Material not conforming to this specification or to authorized modifications will be subject to rejection.

5.0 PREPARATION FOR DELIVERY

5.1 PACKAGING AND PACKING: Unless otherwise specified on the procurement document, all material shall be separated by condition, size and thickness, and packed in crates or boxes of size and construction commonly used for shipment. The crating or boxing shall be such as to insure acceptance by common or other carriers for safe transportation, at the lowest rate, to the point of delivery.

6.0 NOTES

6.1 INTENDED USE - The material covered by this specification is intended for use in the fabrication of airframe parts where strength between 1800°F - 3000°F is required.

6.2 ORDERING DATA - Procurement documents should specify the following:

- (a) Number, title and date of specification
- (b) Condition of material (see 3.2)
- (c) Tolerances, if other than as specified in 3.7

MMS- 184	MOLYBDENUM ALLOY STRIP, SHEET AND PLATE (MOLYBDENUM - 0.5% TITANIUM - 0.07% ZIRCONIUM)	ISSUED 10 July 1961
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FIGURE 1 - RECRYSTALLIZATION REFERENCE STANDARD

ISSUED 10 July 1961 REVISION C 23 January 1964	MOLYBDENUM ALLOY STRIP, SHEET AND PLATE (MOLYBDENUM - 0.5% TITANIUM - 0.07% ZIRCONIUM) STANDARD MATERIAL SPECIFICATION	MMS- 184 PAGE 3 OF 4 CODE IDENT. NO. 76301
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7.0 APPROVED PRODUCTS

Not Applicable.

PROPERTY	GAGE			
	0.010 to 0.025 inc.	Over 0.025 to 0.060 inc.	Over 0.060 to 0.090 inc.	Over 0.090 to 0.187 inc.
Ultimate Tensile Strength Min., psi	140,000	135,000	130,000	130,000
Tensile Yield Strength (0.2% offset), Min., psi	115,000	110,000	105,000	105,000
Elongation, % in 1 and 2 inches, Min.	4%	5%	7%	8%

TABLE I - ROOM TEMPERATURE TENSILE PROPERTIES

TEST TEMPERATURE	1800°F	2000°F	2200°F	2400°F *	2700°F*	3000°F*
Ultimate Tensile Strength Min.	70,000 psi	60,000 psi	50,000 psi	18,000 psi	12,000	7,000
Tensile Yield Strength (0.2% offset) Min.	35,000 psi	30,000 psi	25,000 psi	9,000 psi	6,000	3,000
Elongation, % in 1 and 2 Inches, Min.						
.010 - .025 in.	4	4	5	12	15	20
over .025 - .060 in.	5	5	6	15	20	25
over .060 - .090 in.	6	6	8	20	25	25
over .090 - .187 in.	7	7	10	20	25	25

NOTES: High temperature tensile specimens shall be free from contamination after test.
 Mechanical properties for 2700°F & 3000°F are for reference only, not guaranteed.
 * To be tested in the fully recrystallized condition.

TABLE II - ELEVATED TEMPERATURE TENSILE PROPERTIES

Vendors or subcontractors needing this specification should direct their request for copies to the attention of MAC Purchasing or Subcontracting, as applicable. Information pertaining to the technical aspects of this specification can be obtained from MAC Material and Process Development (Dept.272).

PREPARED M. Deutch

APPROVED C. Fugua
Engineering

MMS- 184	MOLYBDENUM ALLOY STRIP, SHEET AND PLATE (MOLYBDENUM - 0.5% TITANIUM - 0.07% ZIRCONIUM)	ISSUED 10 July 1961
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APPENDIX B

PRODUCT SPECIFICATION FOR NIOBIUM ALLOYS

WAH CHANG ALBANY

ISSUED: July 24, 1970

COLUMBIUM ALLOYColumbium Alloy Plates, Sheets, and Strip

1. SCOPE

1.1 Scope. This specification establishes the requirements for Columbium alloy plates, sheets, and strip.

1.2 Classification. Columbium alloy plates, sheet, and strip procured to this specification shall be supplied in the following types.

<u>Type</u>	<u>Composition</u>
Cb	Cb
WC103	Cb - 10Hf - 1Ti
WC129Y	Cb - 10Hf - 10W - .1Y
Cb-1Zr	Cb - 1Zr
Cb 752	Cb - 10W - 2.5Zr.

2. APPLICABLE DOCUMENTS

2.1 The following documents of the issue in effect on the date of invitation for bids or request for proposal, form a part of this specification to the extent specified herein.

STANDARDS

Federal

Federal Test Method
Standard No. 151

Metals; Test Methods

MIL STD 271

Non-Destructive Testing, (X-ray, Sonics,
Dye Penetrant)American Society for Testing Materials

ASTM-E112

Methods for Determining Average Grain Size.

ISSUED: July 24, 1970

COLUMBIUM ALLOY

Plate, Sheet, and Strip

National Academy of Science

Material advisory board
MAB-216-M

Evaluation Test Methods for Refractory
Metal Sheet Material

Aeronautical Material Specifications

AMS 2242a

Tolerances

3. REQUIREMENTS

3.1 Materials

3.1.1 Production Methods. The ingot metal shall be double Vacuum melted in a furnace of a type suited for reactive metals. The starting ingot shall be free of voids and defects as determined by ultrasonic inspection.

3.1.2 Alloy Identification. The identity of all alloys with respect to ingot melt number shall be maintained at all stages of fabrication.

3.1.3 Condition. Unless otherwise specified, all material shall be supplied in the recrystallized annealed condition in accordance with Table I.

TABLE I

<u>Thickness</u>	<u>% Recrystallization</u>				
	<u>Cb*</u>	<u>WC103</u>	<u>WC129Y</u>	<u>Cb-1Zr</u>	<u>Cb752</u>
Less than .005	A/W	A/W	A/W	A/W	A/W
.005 - .150	A/W	95 - 100%	95 - 100%	95 - 100%	95 - 100%
.151 - .250	A/W	90 - 100%	90 - 100%	90 - 100%	90 - 100%
.251 - 1.00	A/W	85 - 100%	85 - 100%	85 - 100%	85 - 100%

*Material supplied in the As Worked (A/W) condition unless otherwise specified by the P/O.

3.2 Chemical Composition. The Chemical Composition of each alloy ingot shall conform to Table II.

ISSUED: July 24, 1970

COLUMBIUM ALLOY

Plate, Sheet, and Strip

TABLE II

<u>Element</u>	<u>Cb</u>	<u>WC103</u>	<u>WC129Y</u>	<u>Cb-1Zr</u>	<u>Cb752</u>
Tungsten	500 ppm*	5000 ppm*	9 - 11%	500 ppm*	9 - 11%
Hafnium	---	9 - 11%	9 - 11%	200 ppm*	2000 ppm*
Tantalum	1000 ppm*	5000 ppm*	5000 ppm*	1000 ppm*	5000 ppm*
Yttrium	---	---	.05 - .3%	---	---
Titanium	---	.7 - 1.3%	---	---	---
Zirconium	500 ppm*	7000 ppm*	5000 ppm*	.8 - 1.2%	2.0 - 3.0
Carbon	100 ppm*	150 ppm*	150 ppm*	200 ppm*	150 ppm*
Oxygen	150 ppm*	225 ppm*	225 ppm*	300 ppm*	225 ppm*
Nitrogen	100 ppm*	100 ppm*	100 ppm*	100 ppm*	100 ppm*
Hydrogen	15 ppm*	15 ppm*	15 ppm*	15 ppm*	15 ppm*
Columbium	Bal.	Bal.	Bal.	Bal.	Bal.

*Maximum limits unless otherwise indicated.

ppm = Parts Per Million.

3.2.1 Product Analysis. If specified, product analysis shall be performed on C, O₂, N with maximum levels specified as follows on Parts Per Million (ppm).

<u>Element</u>	<u>Cb</u>	<u>WC103</u>	<u>WC129Y</u>	<u>Cb-1Zr</u>	<u>Cb752</u>
C	100	150	150	200	150
O ₂	150	225	225	300	225
N	100	100	100	100	100

3.3 Tensile Properties. Elongation, yield strength, and ultimate tensile strength shall be measured at room temperature on samples transverse to final rolling direction on material which is 0.010" thick or greater. The strain rate shall be maintained at 0.005 ± 0.001"/per inch/per minute through the 0.2% offset yield strength and at 0.05 ± 0.005"/per inch per minute thereafter. The material shall have minimum transverse tensile property values as specified in Table III.

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Plate, Sheet, and Strip

TABLE III

	<u>Cb</u>	<u>WC103</u>	<u>WC129Y</u>	<u>Cb-1Zr</u>	<u>Cb-752</u>
Ultimate tensile strength, 1000 psi	--	54	80	35	75
Yield strength, 0.2% offset, 1000 psi	--	40	60	15	55
Elongation, % in one inch	--	20	20	20	20

3.4 Bend Ductility. Representative samples of the materials in final form shall withstand the following bend test at room temperature without failure when tested according to procedures described in the most recent revision of the Materials Advisory Board report MAB-216-M, "Evaluation Test Methods for Refractory Metal Sheet Materials". The samples shall be sectioned with the long axis of the bend specimens perpendicular to the final rolling direction.

3.4.1 Sheet 0.060" in thickness and under shall be bent over a 1T radius through 105 degrees at a ram speed of one inch/per minute.

3.4.2 Sheet over 0.060" to 0.187" in thickness shall be bent over a 2T radius through 105 degrees at a ram speed of one inch/per minute.

3.5 Grain Size. Unless otherwise specified, the minimum average ASTM grain size number shall be in accordance with Table IV.

TABLE IV

<u>Thickness</u>	<u>WC-103</u>	<u>WC-129Y</u>	<u>Cb-1 Zr</u>	<u>Cb-752</u>
.006 - .150"	6	6	5	6
.151 - .500"	5	5	4	5
Greater than .750"	--	--	--	--

4. DIMENSIONS AND TOLERANCES

4.1 Dimensions and Tolerances. Unless otherwise specified, tolerances shall be as defined in AMS 2242a.

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Plate, Sheet, and Strip

4.2 Flatness. Total deviation from flatness of sheet and strip shall not exceed 6% as determined by the following formula:

$$\frac{H}{L} \times 100 = \text{percent of flatness deviation.}$$

where H = maximum distance from a flat reference surface,
and L = minimum distance from this point to the point of
of contact with the reference surface.

4.3 Marking for Identification. Each plate, sheet, and strip shall be suitably marked with the contract number or order number, ingot melt number, specification number, and composition number.

5. QUALITY

5.1 General. The finished product shall be visibly free from oxide or scale of any nature, grease, oil residual lubricants, and other extraneous materials. Cracks, laps, seams, gouges, and fins shall be unacceptable.

5.2 Surface Rework. All surface pores, gouges, and other defects deeper than 0.005" or 3% of the thickness, whichever is smaller, shall be unacceptable. Surface imperfections may be faired smooth to remove any notch effect provided dimensional tolerances are still maintained.

5.3 Edge. The edges shall be produced by shearing, slitting or sawing. The burr height shall not exceed five (5) percent of the thickness of the material.

6. REPORTS. The supplier shall submit three certified copies of reports indicating the ingot chemistry. In addition, the material will be certified, but not tested to this specification. Additional tests for tensile, yield, elongation, and grain size, and product analysis for oxygen, carbon, and nitrogen will be furnished when specified in the purchase order.

7. PREPARATION FOR DELIVERY

7.1 Packaging. All material shall be packaged in a manner that will prevent damage in transit and in storage.

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Plate, Sheet, and Strip

8. REJECTIONS. Material not conforming to any of the requirements of this specification unless otherwise agreed upon by the purchaser.

9. DEFINITIONS. For the purposes of this specification, the following definitions shall apply:

9.1 Sheet. Sheet is flat, rolled material up to 0.125" thick, normally supplied in widths over twelve (12)".

9.2 Plate. Plate is flat, rolled material 0.125" thick or greater.

9.3 Strip. Strip is flat, rolled material up to 0.060" thick in widths under twelve (12)".

APPENDIX C

PRODUCT SPECIFICATION FOR Ta-10W ALLOY (FS-60)
FANSTEEL METALS

Fansteel

FANSTEEL METALLURGICAL CORPORATION • NORTH CHICAGO, ILLINOIS

TECHNICAL DATA BULLETIN

METALS DIVISION

TD-60-623-B

PRODUCT SPECIFICATION NO. S-60-S-01-R-0

Date Issued: 6/15/67

FANSTEEL 60 METAL FLAT MILL PRODUCT: Plate, Sheet and Strip

- 1.0 ACKNOWLEDGEMENT: All orders and inquiries shall reference this specification by number.
- 2.0 GRADE: Fansteel 60 Metal is produced by vacuum melting.
- 3.0 CONDITION: Material shall be supplied in the fully recrystallized condition, unless otherwise specified.
- 4.0 COMPOSITION: The material shall conform to the chemical composition as follows:

Applicable Thickness	0.010" to 0.015"	0.016" to 0.055"	0.056" to 0.250"
Element	Maximum	Maximum	Maximum
Carbon	75 ppm	50 ppm	50 ppm
Oxygen	150 ppm	100 ppm	75 ppm
Nitrogen	75 ppm	50 ppm	50 ppm
Hydrogen	10 ppm	10 ppm	10 ppm
Columbium	1000 ppm	1000 ppm	1000 ppm
Iron	75 ppm	75 ppm	75 ppm
Molybdenum	300 ppm	300 ppm	300 ppm
Nickel	50 ppm	50 ppm	50 ppm
Titanium	50 ppm	50 ppm	50 ppm
Cobalt	50 ppm	50 ppm	50 ppm
Vanadium	50 ppm	50 ppm	50 ppm
Tungsten	9.0 - 11.0%	9.0 - 11.0%	9.0 - 11.0%
Tantalum	Balance	Balance	Balance

5.0 TECHNICAL REQUIREMENTS:

5.1 Mechanical Properties

Material supplied under this specification shall conform to the following requirements when tested transverse to the rolling direction as described in Section 9.1.

Thickness Range	0.010" to 0.020"	0.021" to 0.250"
Ultimate Tensile Strength (psi)	75,000 Minimum	70,000 Minimum
Yield Strength 0.2% Offset (psi)	65,000 Minimum	60,000 Minimum
Elongation in 2"	15% Minimum	20% Minimum

All Thicknesses	Maximum	Minimum
Hardness R_A	65	55
R_B	100	90
R_C	20	10

5.2 Recrystallization

Material supplied under this specification shall have a 100% recrystallized microstructure when inspected as described in Section 9.2.

6.0 QUALITY: Material shall be uniform in quality, clean and sound.

6.1 Surface

Surface quality shall be consistent with good commercially rolled sheet. Minor surface defects shall be removed by conditioning. Such conditioning shall be smoothly blended into surfaces and held within allowable thickness tolerances described in Section 7.1.

6.2 Edges

Sheared edges shall be smooth and free of laminations.

7.0 STANDARD TOLERANCES

7.1 Thickness

Material Thickness (Inches)	Tolerance ($\pm$ Inches) Widths to 12" Inclusive
0.010	0.0012
0.015	0.0015
0.020	0.0020
0.025	0.0025
0.030	0.0030
0.040	0.0035
0.050	0.0040
0.060	0.0045
0.090	0.0055
0.125	0.0080
0.126 - 0.250	0.0120

Thickness Tolerances for widths greater than 12" available on request.

7.2 Width

Material Thickness (Inches)	Tolerance (Inches)	
	Widths to 12" Incl.	Widths 12" to 42" Incl.
0.010 - 0.025	$+1/32$ - .000	$+1/16$ - .000
0.026 - 0.100	$+1/16$ - .000	$+1/8$ - .000
0.101 - 0.250	$+1/8$ - .000	$+3/16$ - .000

7.3 Length

Material Thickness (Inches)	Lengths to 96" Incl.*	
	Widths to 12" Incl.	Widths 12" to 42" Incl.
0.010 - 0.015	$+1/32$ - .000	$+1/8$ - .000
0.016 - 0.025	$+1/32$ - .000	$+1/8$ - .000
0.026 - 0.060	$+3/64$ - .000	$+5/32$ - .000
0.061 - 0.100	$+1/16$ - .000	$+3/16$ - .000
0.101 - 0.250	$+1/8$ - .000	$+1/4$ - .000

*Tolerances for lengths greater than 96" exclusive are available upon request.

7.4 Flatness

Flatness tolerance shall be 5% for widths up to 24" inclusive and 6% for widths from 24" exclusive to 42" inclusive. Flatness shall be determined by allowing the sheet to lie freely on flat surface during measurement. Flatness tolerances shall be computed from the following formula:

$$H/L \times 100 = \text{percent flatness}$$

where"

H = the maximum distance between flat surface and the lower surface of the sheet.

L = the minimum distance between the highest point on the sheet and point of contact with the flat surface.

8.0 PRECISION TOLERANCES: Are available upon request.

9.0 TEST METHODS:

9.1 Tensile Test

Representative specimens from each lot of material shall be prepared and tested in conformity with the Tentative Methods of Tensile Testing of Metallic Materials (ASTM-E-8).

Tensile properties shall be determined by using a head speed of 0.02"/min. through 0.2% offset and then 0.2"/min. to fracture. Specimens shall be taken transverse to the final rolling direction. All tests shall be conducted at a temperature between 65°F and 85°F.

Representative specimens from each lot shall be tested for Rockwell Hardness. The Rockwell test shall be made on the "as rolled" surface. A minimum of three (3) tests shall be taken and their average reported for each specimen.

9.2 Structure Tests

Representative specimens from each lot shall be metallographically prepared and checked for microstructure at a magnification of 100 X or above.

9.3 Analytical Method

The following analytical testing methods shall be used to determine:

Carbon	Combustion - Conductometric
Oxygen	Inert-Gas Fusion
Nitrogen	Micro Kjeldahl
Hydrogen	Vacuum Hot Extraction
Metallics	Emission and/or X-Ray Spectrographic

10.0 REPORTS: When specified, Fansteel shall certify and furnish triplicate test reports documenting the billet composition and the technical requirements of the final product. Check analysis for verification of chemical composition of the final product shall be reported only when agreed upon.

APPENDIX D

COMPOSITIONS OF NIOBIUM AND TANTALUM ALLOYS

COMPOSITIONS OF NIOBIUM BASE ALLOYS

<u>Composition</u>	<u>Alloy Designation</u>	<u>Density</u>		<u>Comments</u>
		gm/cm ³	lb/in ³	
Nb	Nb, D10,	8.58	.310	In Production ↓
Nb-1Zr	Nb-1Zr, D11, Cb751 FS-80	8.58	.310	
Nb-10Hf-1Ti-.5Zr	C103	8.96	.324	
Nb-10W-10Hf-.04Y	C129Y	9.49	.343	
Nb-10W-2.5Zr	Cb752	9.02	.326	
Nb-28Ta-10W-1Zr	FS85	10.60	.383	Out of Production ↓
Nb-10W-10Ta	SCb291	9.60	.347	
Nb-5V-1.25 Zr	Cb-753	8.39	.303	
Nb-20W-1Zr .1C	AS-30	9.60	.347	
Nb-5W-1Zr	AS-55	8.77	.317	
Nb-5V	B-33	8.47	.306	
Nb-5Mo-5V-1Zr	B-66	8.44	.305	
Nb-10W-5V-1Zr	B-77	8.66	.313	
Nb-10W-10Hf	C-129	9.46	.343	
Nb-5Ti	D12	8.05	.291	
Nb-5Zr	D14	8.58	.310	
Nb-10Ti-10Mo-.1C	D31	8.08	.292	
Nb-10Ti-5Zr	D36	7.92	.286	
Nb-15W-5Mo-1Zr	D40	9.41	.340	
Nb-10W-2Mo-1Zr	D40M	8.75	.316	
Nb-20W-10Ti-6Mo	D41	8.86	.320	
Nb-10W-1Zr-.1C	D43	9.02	.326	
Nb-15W-5Mo-1Zr	F48	9.41	.340	
Nb-15W-5Mo-5Ti-1Zr	FS50	9.13	.330	
Nb-32Ta-1Zr	FS82	10.16	.367	

COMPOSITIONS OF TANTALUM BASE ALLOYS

<u>Composition</u>	<u>Alloy Designation</u>	<u>Density</u>	
		gm/cm ³	lb/in ³
Ta	Ta	16.61	.600
Ta-10W	FS60	16.82	.608
Ta-8W-2Hf	T111	16.72	.604
Ta-10W-2.5Hf	T222	16.72	.604
Ta-7.5W	FS-61	16.82	.608
Ta-8W-3Re	GE-473	16.91	.611

APPENDIX E

CONVERSION OF U.S. CUSTOMARY UNITS TO SI UNITS

APPENDIX E

CONVERSION OF U.S. CUSTOMARY UNITS TO SI UNITS

The International System of Units (designated SI) was adopted by the Eleventh General Conference on Weights and Measures in 1960. The units and conversion factors used in this report are taken from or based on IASA SP-7012, "The International System of Units, Physical Constants and Conversion Factors - Revised, 1973".

The following table expresses the definitions of miscellaneous units of measure as exact numerical multiples of coherent SI units, and provides multiplying factors for converting numbers and miscellaneous units to corresponding new numbers of SI units.

The first two digits of each numerical entry represent a power of 10. An asterisk follows each number that expresses an exact definition. For example, the entry "-02 2.54*" expresses the fact that 1 inch = 2.54×10^{-2} meter, exactly, by definition. Most of the definitions are extracted from National Bureau of Standards documents. Numbers not followed by an asterisk are only approximate representations of definitions, or are the results of physical measurements.

ALPHABETICAL LISTING

<u>To convert from</u>	<u>to</u>	<u>multiply by</u>
atmosphere (atm)	pascal (Pa)	+05 1.0133*
Fahrenheit (F)	kelvin (K)	$t_k = (5/9) (t_f + 459.67)$
foot (ft.)	meter (m)	-01 3.048*
inch (in.)	meter (m)	-02 2.54*
mil	meter (m)	-05 2.54*
millimeter of mercury (mm Hg)	pascal (Pa)	+02 1.333
nautical mile, U.S. (n.mi.)	meter (m)	+03 1.852*
pound force (lbf)	newton (N)	+00 4.448*
pound mass (lbm)	kilogram (kg)	-01 4.536*
torr (0°C)	pascal (Pa)	+02 1.333

PHYSICAL QUANTITY LISTING

<u>Area</u>		
<u>To convert from</u>	<u>to</u>	<u>multiply by</u>
foot ² (ft ²)	meter ² (m ²)	-02 9.290*
inch ² (in ²)	meter ² (m ²)	-04 6.452*
inch ² (in ²)	centimeter ² (cm ²)	+00 6.452

APPENDIX E - Continued

PHYSICAL QUANTITY LISTING

<u>To convert from</u>	<u>Density</u> <u>to</u>	<u>multiply by</u>
pound mass/foot ³ (pcf, lbm/ft ³)	kilogram/meter ³ (kg/m ³)	+01 1.602
pound mass/inch ³ (lbm/in ³)	kilogram/meter ³ (kg/m ³)	+04 2.768
pound mass/inch ³ (lbm/in ³)	gram/centimeter ³ (g/cm ³)	+01 2.768

	<u>Force</u>	
kilogram force (kgf)	newton (N)	+00 9.807*
pound force (lbf)	newton (N)	+00 4.448*

	<u>Length</u>	
foot (ft)	meter (m)	-01 3.048*
inch (in.)	meter (m)	-02 2.54*
micron	meter (m)	-06 1.00*
mil	meter (m)	-05 2.54*
mile, U.S. nautical (n.mi.)	meter (m)	+03 1.852*

	<u>Mass</u>	
pound mass (lbm)	kilogram (kg)	-01 4.536*

	<u>Pressure</u>	
atmosphere (atm)	pascal (Pa)	+05 1.013*
millimeter of mercury (mm Hg)	pascal (Pa)	+02 1.333
newton/meter	pascal (Pa)	00 1.00*
pound/foot ² (psf, lbf/ft ²)	pascal (Pa)	+01 4.788
pound/inch ² (psi, lbf/in ²)	pascal (Pa)	+03 6.895

	<u>Temperature</u>	
Fahrenheit (F)	Kelvin (K)	$t_k = (5/9)(t_f + 459.67)$

	<u>Volume</u>	
foot ³ (ft ³)	meter ³ (m ³)	-02 2.832*
inch ³ (in ³)	meter ³ (m ³)	-05 1.639*
inch ³ (in ³)	centimeter ³ (cm ³ , cc)	01 1.639

APPENDIX E - Continued

PREFIXES

The names of multiples and submultiples of SI units may be formed by application of the prefixes:

Multiple	Prefix
10^{-6}	micro (μ)
10^{-3}	milli (m)
10^{-2}	centi (c)
10^{-1}	deci (d)
10^3	kilo (k)
10^6	mega (M)
10^9	giga (G)

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