PRODUCIBILITY OF AN ALLOY OF COLUMBIUM WITH ONE PERCENT ZIRCONIUM

Prepared By: L.M. RARING

UNCLASSIFIED
CLASSIFICATION

J.R. Miller
AUTHORIZED CLASSIFIER

December 9, 1959
DATE

INTRODUCTION

A comprehensive metallurgical and engineering evaluation of the columbium-one percent zirconium alloy conducted by Pratt & Whitney Aircraft, CANEL, over the past 18 months, necessitated the melting, fabrication, and joining of relatively large quantities of material for specific test purposes. During the course of this program, considerable work was accomplished in the development and improvement of techniques for consolidation, working, and joining of this new alloy. This report is intended to summarize briefly the major supporting data which demonstrate the producibility of the alloy for engineering structural applications. The report is therefore confined to a brief review of ore resources, extraction and melting capacities, and major achievements in melting, hot and cold working, fabrication, and joining of the alloy.

SUMMARY

Proven mineral resources show that columbium is the most abundant of the refractory metals and extraction capacity is adequate to meet foreseeable requirements. Approximately four tons of columbium-one percent zirconium alloy have been melted, forged, drawn, and rolled to produce various mill forms and relatively large die impression forgings. It has been demonstrated that the columbium-one percent zirconium alloy is readily amenable to melting, primary working, and secondary working using standard equipment available in the specialty steel and nickel alloy industries. In general, the hot malleability of the alloy is significantly better than that of the more refractory nickel base high temperature alloys and is comparable to the stainless steels. Methods have been successfully developed to protect the alloy against contamination during hot working.

Cold fabricability has proven to be outstanding. Reductions up to 90 percent are achieved during cold rolling of sheet with no intermediate stress relief or annealing treatment. Tube drawing reductions up to 50 percent are normal with no intermediate annealing. Over-all, the cold workability of this alloy is superior to that of the stainless steels. There has been no problem of embrittlement over the full range of working temperatures which has been used during the course of this work, namely from room temperature to 2350F.

Welding of the columbium-one percent zirconium alloy has been developed to the stage where many thousands of welds have been performed in a routine manner with insignificant rejections.

COLUMBIUM RESOURCES

Columbium has experienced a rapid transition from a scarce metal under strict Government control in 1952 to one of relative abundance in 1958. This has been due to intensive ore exploration and the discovery of large ore bodies in various parts of the world. Fig 1 compares the known free world ore resources in terms of contained metal for the most promising refractory metals, tungsten, tantalum, vanadium, molybdenum, and columbium. A total of seven million tons of contained metal have been estimated for columbium whereas less than three million tons have been proven in the case of molybdenum. From the standpoint of known ore resources, columbium is the most abundant of the refractory metals.

The most important ores of columbium at the present time are the columbites (FeMn) Cb_2O_5 which generally occur with tantalite (FeMn) Ta_2O_5. A more abundant mineral resource occurs in the form of pyrochlore which is essentially a calcium columbate. This mineral has a much higher columbium-tantalum ratio than the columbite ores.

The principle deposits of columbite in the free world occur in Nigeria, the Belgian Congo, and Malaya. Large pyrochlore deposits occur in Nigeria, Uganda, Tanganyika, Kenya, Northern Rhodesia, Nyasuland, Brazil, Canada, Norway, and the United States. Commercial development of the Tanganyika and Uganda pyrochlores are in an advanced stage. Other deposits are in the pilot plant stage. The Brazilian deposits are the richest known.

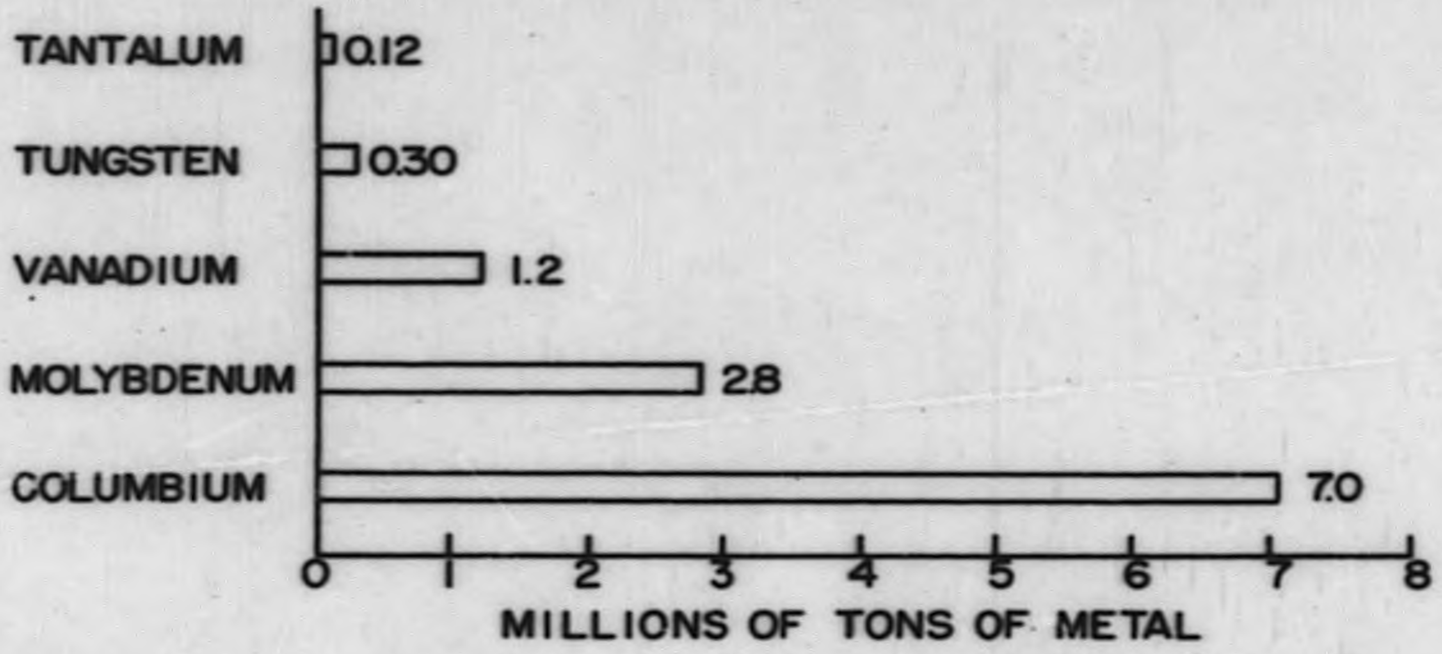
There are additionally, in ready reserve, approximately 6,000 tons of columbium oxide concentrates available between the United States government stockpile and the by-product concentrate accumulated through tantalum production over the past years.

EXTRACTION

Ore concentrates are prepared by conventional gravity methods, utilizing sluice boxes, jigs, and tables followed sometimes by magnetic and electrostatic separation. Tantalum is separated by liquid-liquid extraction, fractional crystallization, fractional distillation, or ion exchange. Reduction of columbium metal from ore concentrates is accomplished by several methods. Carbon reduction of the oxide is widely used and, in addition, reduction of the chloride by magnesium, sodium or calcium is feasible. There are several proprietary methods which are said to be capable of producing very high purity metal.

Present extraction capacity in the United States is capable of an annual production rate of 175,000 pounds of pellet or powder metal suitable for consolidation to massive form by melting or powder pressing and sintering. A survey of the major producers has indicated that, with only minor capital costs, this rate could be increased to approximately 800,000 pounds. Assuming a conservative conversion yield, this is equivalent to 400,000 pounds of mill product.

METAL CONTENT OF KNOWN FREE WORLD ORE RESOURCES OF SEVERAL REFRACTORY METALS



REF: MAB REPORT NO. MAB-154-M

CNLM · 2:66
FIG 1

MELTING

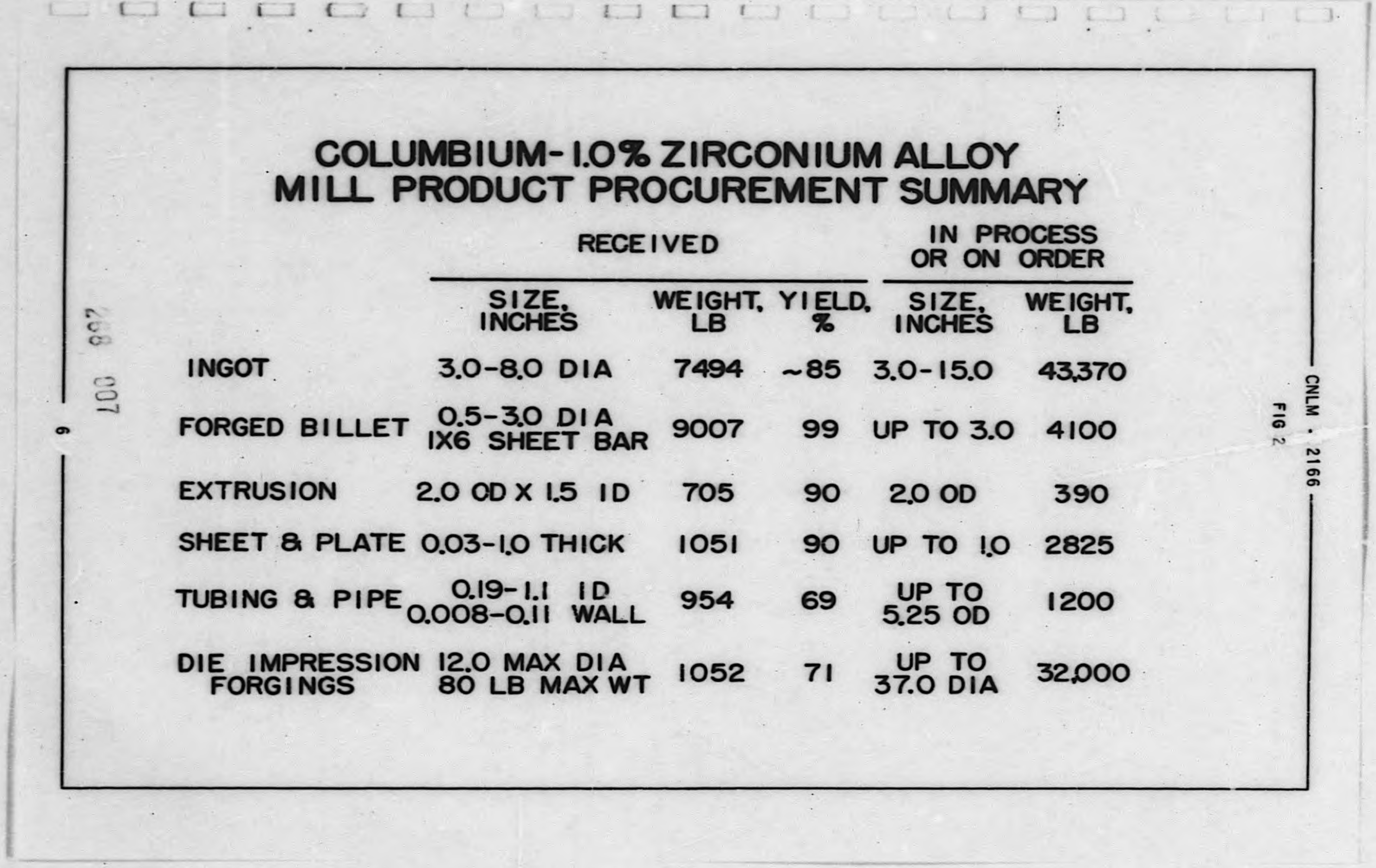
At the time the Pratt & Whitney Aircraft program was undertaken, early in 1958, very little work had been done in the arc melting of columbium or its alloys. Several laboratories had been producing nonconsumable melts of "pure" metal or alloys in the form of "pancake" melts of several hundred grams weight for evaluation. Reports from the few laboratories that had attempted the arc melting of ingots of two or three inch diameter by the "consumable" process were discouraging. Generally, these ingots were quite hard, owing to high impurity levels, and difficult to forge to bar or roll into sheet. For this reason, the first tubing samples which were obtained for the initial liquid metal corrosion tests, had to be produced by the powder metallurgy route, that is, by pressing powder, sintering, drilling, and cold drawing. This tubing was of generally unsatisfactory quality. This problem was solved by employing electron beam melting which, because of the higher vacuums obtainable, produced ingots of considerably greater purity than that which could be obtained by conventional arc melting. A melting process was developed which took advantage of the purification achieved by electron beam melting of relatively impure starting material as an initial melting step. Subsequent remelting by the conventional vacuum arc process was then used to produce larger diameter ingots as required for fabrication of large forgings.

During the past eighteen months, a total of roughly 7500 pounds of columbium-one percent zirconium ingot has been melted by this "duplex" melting process. In addition, approximately 10,000 pounds of pure columbium and columbium alloys other than the one percent zirconium alloy have been similarly melted to ingot. Fig 2 summarizes ingot production. This figure shows an additional 43,370 pounds currently in process. The ingot sizes, as shown in Fig 2, have ranged between 3.0 and 8.0 inches. In addition, a 12.0 inch diameter ingot has been melted and applied successfully to large die impression forgings. Melting now in progress include ingot sizes to 15 inches diameter. Fig 3 shows two 8 inch ingots after cropping and turning.

Melting yields, or the ratio of "cleaned-up" weight to "as-cast" weight is in the order of 85 percent. The 15 percent losses include "cropping" the top and bottom of the ingots and lathe turning the surface to provide a clean, sound piece for subsequent hot reduction. This yield is in accord with yields obtained in the melting of titanium, zirconium, and the commercial nickel base alloys.

Arc melting capacity in the United States includes the titanium and zirconium melting facilities as well as the specialty steel and nickel base alloy melters. Facilities for arc melting have been increasing at a very rapid rate over the past five years. The titanium industry alone possesses an arc melting capacity of 40,000 tons per year. The combined facilities of the specialty steel and nickel alloy producers greatly exceeds this figure. Power capacity is available for melting ingots up to 20 inches in diameter.

The electron beam melting capacity in the United States is at the 150 to 200 tons per year level now and additional facilities are being built. Further refinement in extraction methods to provide purer starting material may minimize the need for electron beam purification in the future. In any case, the present capacity for production melting of high purity columbium-one percent zirconium alloy is fully capable of meeting foreseeable needs.



COLUMBIUM-1.0% ZIRCONIUM ALLOY MILL PRODUCT PROCUREMENT SUMMARY

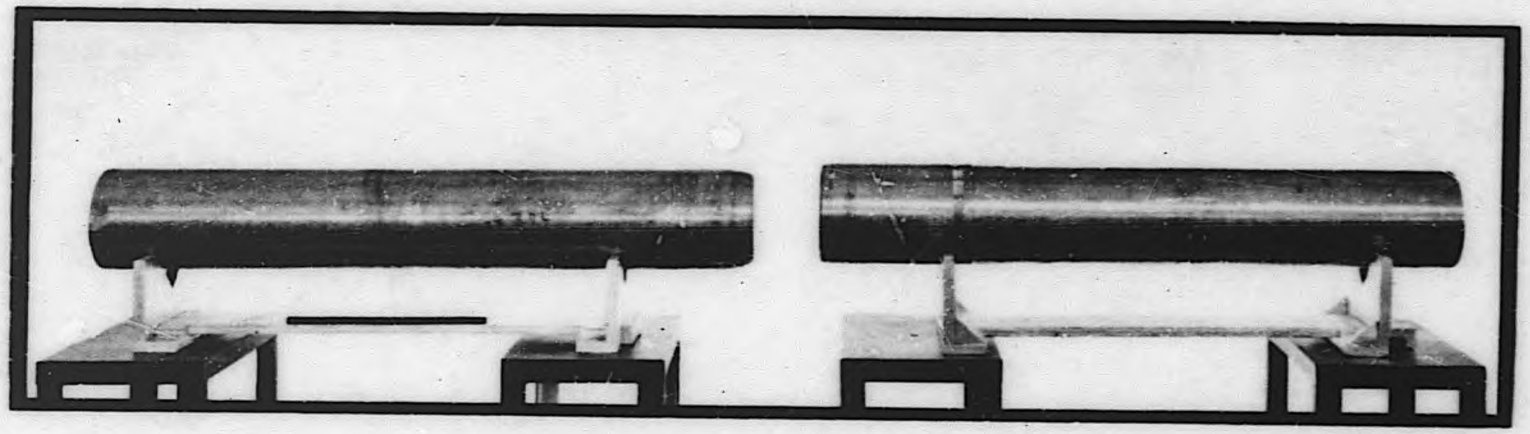
	RECEIVED			IN PROCESS OR ON ORDER	
	SIZE, INCHES	WEIGHT, LB	YIELD, %	SIZE, INCHES	WEIGHT, LB
INGOT	3.0-8.0 DIA	7494	~85	3.0-15.0	43,370
FORGED BILLET	0.5-3.0 DIA 1X6 SHEET BAR	9007	99	UP TO 3.0	4100
EXTRUSION	2.0 OD X 1.5 ID	705	90	2.0 OD	390
SHEET & PLATE	0.03-1.0 THICK	1051	90	UP TO 1.0	2825
TUBING & PIPE	0.19-1.1 ID 0.008-0.11 WALL	954	69	UP TO 5.25 OD	1200
DIE IMPRESSION FORGINGS	12.0 MAX DIA 80 LB MAX WT	1052	71	UP TO 37.0 DIA	32,000

CNLM - 2166

FIG 2

VACUUM ARC MELTED INGOTS

COLUMBIUM- 1.0% ZIRCONIUM ALLOY   8 INCH DIAMETER



589 POUNDS   539 POUNDS

CNLM - 2166
FIG 3

PRIMARY WORKING

An extensive background of practical experience has been amassed during the past eighteen months in the working of the columbium-one percent zirconium alloy. Fig 2 includes a summary of the total production of forged billet and extrusions. A total of nearly 10,000 pounds of forged and extruded billet has been produced from ingot with yields in excess of 90 percent. This yield figure represents the ratio of billet weight to starting weight and thus reflects the negligible incidence of cracking which was encountered in hot working. Most importantly, this conversion of ingot to billet was accomplished with standard forge shop equipment such as the 5,000 pound steam hammer shown in Fig 4 and conventional extrusion presses. Furthermore, temperatures used in these conversion operations were in the normal range of forge shop furnaces. It was found that ingot conversion could be accomplished at any temperature within the range which was explored, namely 1800F to 2400F. A temperature range of 2100F to 2350F was selected as most suitable after much experience had been gained.

Fig 5 compares results of single blow hot hammer tests at various temperatures for type 316 stainless steel, Inconel, Inconel X, and the columbium-one percent zirconium alloy. It is obvious that the malleability of the columbium alloy is superior to Inconel X, a widely used nickel base alloy, at all temperatures. The slight edge cracking evident on the bare columbium alloy was caused by a superficially contaminated skin which was formed during heating in air prior to the forge test. The coated columbium alloy specimens are entirely free of this shallow edge cracking.

Several practical, inexpensive methods have been developed for protection of the columbium alloy during heating for forging. Special ceramic coatings have proven to be very effective. Most of the production work, however, has been jacketed in low carbon steel prior to heating and forging to protect the columbium alloy against oxidation and surface contamination. These measures obviate the necessity for heating in vacuum or inert gas atmospheres, thus greatly decreasing equipment costs and permitting use of straight forward forge shop equipment and practices.

SECONDARY WORKING

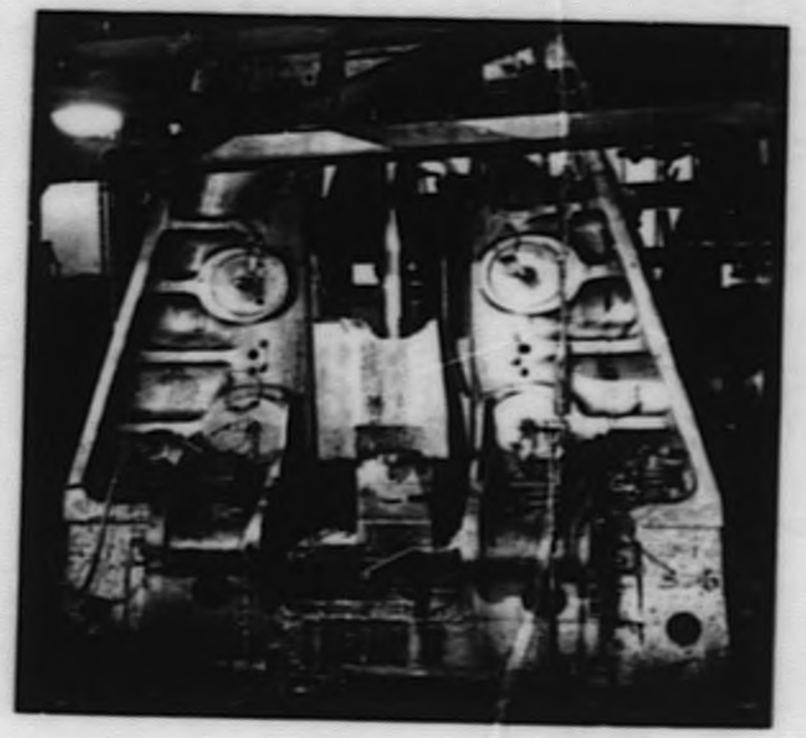
Referring again to Fig 2, it is seen that sheet and plate, tubing, pipe, and die impression forgings have all been successfully produced with yields equal to or exceeding those normally anticipated in secondary working of titanium, zirconium, and the more fabricable nickel and iron base alloys.

The roughly 1000 pounds of sheet and plate were produced by cold rolling using standard roll equipment. Surface quality and tolerances have been extremely good with no evidence of laminations such as has plagued the molybdenum sheet program. One fact which has distinguished this sheet rolling accomplishment has been the ability of the alloy to cold reduce with no stress relief or, at most, only one intermediate stress relief treatment. For example, the sheet production included in Fig 2 was cold rolled from 7/8 inch thick sheet bar to thicknesses as low as

FIG 4

WYMAN - GORDON STEAM HAMMER

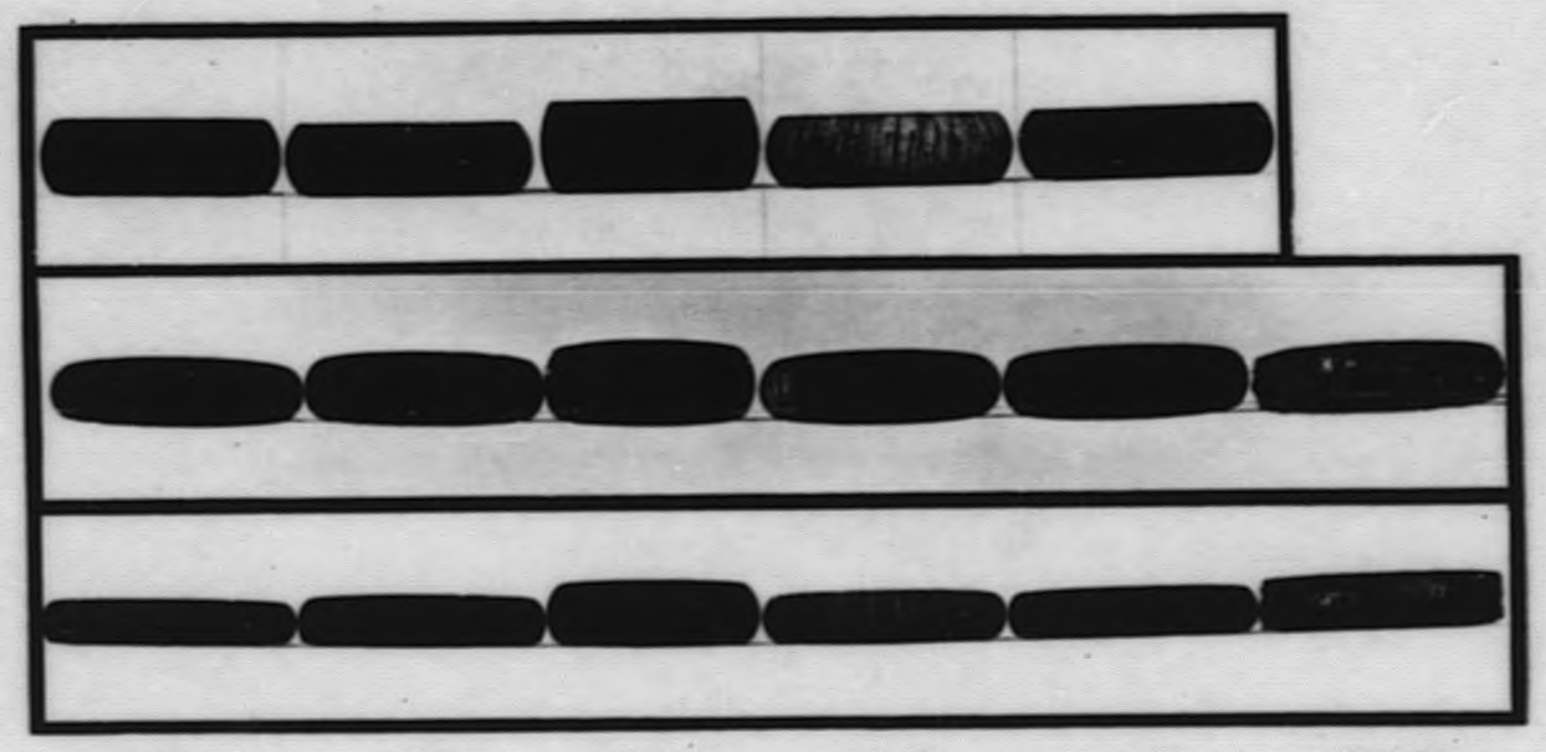
RATED AT 5000 LB FOR INGOT FORGING



268 010

COMPARISON OF HOT WORKABILITY OF Cb-1.0 Zr ALLOY WITH IRON AND NICKLE BASE ALLOYS

SINGLE BLOW HOT UPSET FORGE TEST



ORIGINAL SECTIONS 1 INCH DIAMETER BY 1 INCH HIGH

HAMMER - 500 LBS. 18 INCH DROP

CNLM - 2166

FIG 5

0.030 inch with no stress relief. Warm rolling (600F) has also been done but is not necessary since, unlike molybdenum, chromium, and tungsten, columbium has a very low (less than -180F) ductile-to-brittle transition temperature, and retains excellent ductility in the fully recrystallized state.

Tubing production, as shown in Fig 2, has been proven by the production of 954 pounds of relatively fine tubing with normal yields. The total length, represented by this weight, is roughly in the range of 4,000 feet. Considerable product development has gone into this work but no serious difficulties have been encountered. Vacuum stress relief annealing equipment, available in the case of one prominent producer, has been utilized in processing from tube blanks to finished tube sizes.

Tube drawing practices have been developed which are capable of production of high quality tubing as determined by sensitive nondestructive tests such as ultrasonic reflection, magnetic analysis, radiography, and fluorescent penetrant.

Die impression forgings provide another severe test of the practicability of any alloy considered for structural applications. The columbium-one percent zirconium alloy met this test on the first attempt, without an expensive, time consuming scale-up program. Based upon the knowledge gained on primary ingot conversion to billet, previously described, an attempt was made to go directly to the rather complicated, deep draft, circular forgings shown in Fig 6. The "as-forged" diameter of these pieces was nearly 12 inches. Using the same temperatures (2100F to 2300F) as previously proven on straight ingot cogging on flat or swaging dies, these forgings were produced successfully on the first attempt. The starting billets were upset to pancakes, in the case of the "heads", and then forged in the die to produce the shapes shown. The right cylinder was ring rolled from a punched billet and the flange subsequently upset in a set of forging dies. All forgings were filled out satisfactorily and showed no defects on rigorous nondestructive inspection. These pieces are presently in the semifinished machined condition.

Again, equipment used in the production of these forgings represented standard shop furnaces, hammers, and presses. Fig 7 shows a 7700 ton press which was used in the production of one of the heads. Hammer forging, using a standard 15,000 pound steam hammer, was also employed to gain experience and to compare equipment effects. No special heating equipment was used. Protection against oxidation and contamination during heating to 2300F was provided by either ceramic coatings or low carbon steel jackets. The coatings were found to be superior and the jacketing approach was consequently discontinued. Fig 2 summarizes the total forging weight thus far successfully produced and indicates the scale of work currently in process.

Finally, wire drawing of the columbium-one percent zirconium alloy has been well established during the course of production of several thousand feet of wire for use in welding.

IO INCH PRESSURE VESSEL FORGINGS

COLUMBIUM - I.0% ZIRCONIUM ALLOY

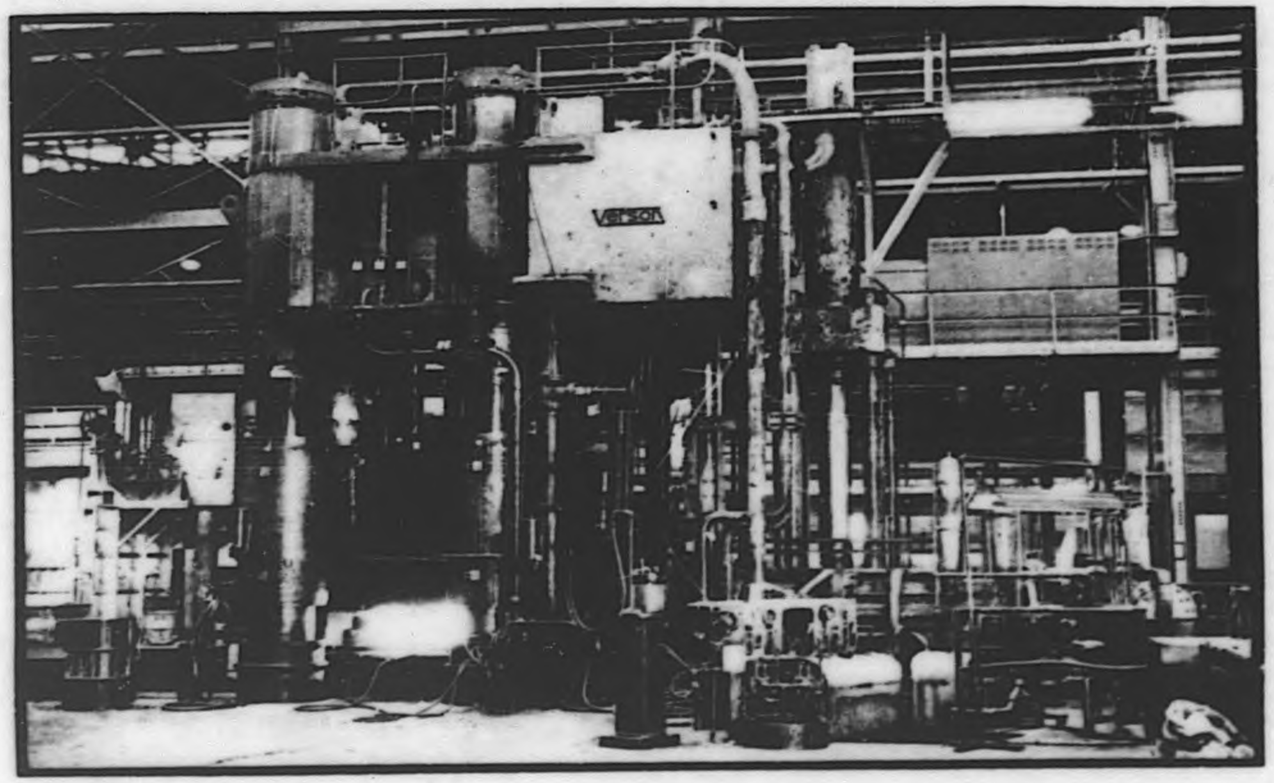
CNLM - 2166

FIG 6

268 013

WYMAN-GORDON 7700 TON PRESS

USED FOR FORGING 10 INCH UPPER HEADS



CNLM - 2166

FIG 7

JOINING

Another basic capability which must be demonstrated by a structural alloy candidate is good weldability. This is required to permit assembly of detailed parts to provide the complex configurations needed in structural design.

The columbium-one percent zirconium alloy has proven to be readily weldable using standard techniques developed for the joining of titanium, zirconium, and molybdenum. Using an inert gas atmosphere, thousands of high quality welds have been made in a variety of section thicknesses and shapes. Close quality inspection by means of radiographic and fluorescent penetrant testing has demonstrated that weld quality is very good and rejection rates are similar to rates normally anticipated in manual welding operations on stainless steels.

Fig 8 shows a production inert gas weld operation in a "dry box" in the left picture. On the right, an experimental welding operation is shown in which the weld is performed in the open, using a special argon shielding manifold which floods the welded region with inert gas. Many high quality welds have been produced by this method which, of course, eliminates the necessity for costly equipment. This development has been highly encouraging thus far and it is anticipated that a considerable volume of shop welding will be carried out in this manner.

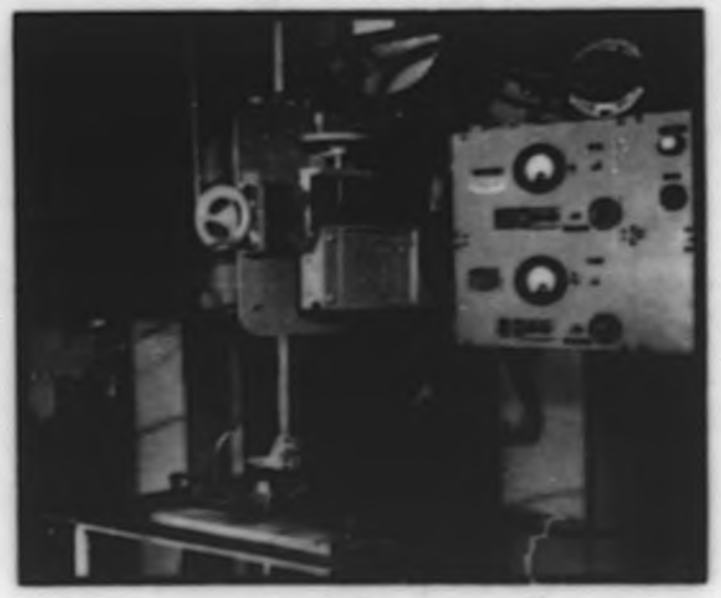
Brazing of columbium-one percent zirconium to itself as well as to dissimilar metals has been done on an experimental production basis in the fabrication of test apparatus. Several thousand brazed joints have been made successfully between the columbium alloy and stainless steels by using standard nickel base braze alloys. A zirconium base braze alloy has been developed which is entirely satisfactory for the brazing of the columbium alloy to itself.

FORMING AND MACHINING

The columbium-one percent zirconium alloy has been proven in a wide variety of machine shop operations such as drilling, turning, grinding, milling, shaping, and electrostatic cutting. Parts have been formed successfully by hydroforming, stamping, shearing, flo-turning, and tube reducing.

COLUMBIUM ALLOY WELDING TECHNIQUES

FUSION ARC WELDING IN ARGON ATMOSPHERE CHAMBER



SEMI-AUTOMATIC WELDING USING AN EXPERIMENTAL ARGON SHIELDING MANIFOLD

CNLM - 2166
FIG 8

GENERAL REMARKS

The information included in this report is based upon actual development experience in the successful production of significant quantities of raw material, semifinished and finished mill shapes, machined details, and test structures. This program has progressed from a state of no real experience to an essentially fully developed production capability in less than two years. As an essential metallurgical and engineering phase of this program, all production operations have been subjected to rigorous metallurgical quality tests to appraise the effect of manufacturing variables on chemical analysis, mechanical properties, and physical quality of the product. The production processes described in this report were developed with engineering quality standards in foremost view. Mill products were checked closely to determine suitability for the intended part. Specifications have been prepared covering ingot, tubing, sheet, and forgings which prescribe quality and engineering properties. The requirements at these specifications have been fully met by the production methods which have been established during this program.