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CURRENT STATUS OF REFRACTORY METALS FOR STRUCTURAL APPLICATIONS

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INTRODUCTION

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This paper is essentially a report on applied research programs which cover the use of refractory materials as load-carrying primary structural members. The Dyna-Soar glider employs refractory materials in leading edges and heat-shield applications. In order to provide growth capability in the Dyna-Soar glider, higher temperature load-carrying structures would be desirable. This paper is a status report on efforts to achieve this goal. In recent months the Wright Air Development Division (WADD) has been cognizant of an urgent need for immediate development in refractory materials for both structural and heat-shield applications and, since no one had really explored the state of the art in refractory metals structural technology, it was decided that fairly comprehensive programs in this area should be initiated. Figure 1 depicts a nominal trajectory including transient conditions for a typical skip reentry mission.

DISCUSSION

WADD began a number of research and development efforts including a contract with McDonnell Aircraft Corporation for the design, fabrication, and test of a representative, refractory metal, load-carrying, structural component capable of efficient operation in the temperature range of 1,800° F to 2,500° F. The General Electric Company, Flight Propulsion Laboratory Division (Evendale, Ohio), was subsequently selected as the main subcontractor. There are two other subcontractors, that is, Hughes Tool Company (Culver City, Calif.), and Temco (Dallas, Texas). This program was aimed at determining the state of the art and demonstrating the feasibility of a refractory metal structure.

It is widely known that one of the primary requirements to produce a refractory metallic end item, having high integrity, is to begin with closely controlled extraction, refinement, melting, and ingot casting practices. Even if the ore is extracted and refined carefully and a

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high purity sponge or other metallic form is obtained many problems remain. An example of one of these problems is conversion of the metal to a powder with which to make ingots for further processing. All refractory metals have an affinity for one or more elements which adversely affect the base metal properties. As a rule undesirable oxides, hydrides, nitrides, etc., may be formed and more often than not, it is necessary to vacuum-arc melt the powder ingot (billet) to purify it. Naturally, the impurity problem does not end here.

Another serious problem is segregation. Because of wide differences in resistivity, conductivity, constituent melting points, and vapor pressures, intolerable differences in chemistry, density, etc., may exist from section to section within the same ingot. This problem has not yet been overcome by powder metallurgy, but it is believed that a properly conducted program on prealloying of powder can greatly alleviate this problem. Also, the undesirable large grain size that is characteristic of cast ingots can be somewhat overcome, initially, through powder metallurgy techniques.

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Next, before the ingot can be processed into bar for machining, or still further processed into sheet, the cast structure must be broken down and the ingot partially homogenized by hot work. Here, again, problems are faced of an entirely different nature. As has been the experience with Al, Mg, Ti, and steel, in order to achieve the ultimate in physical and mechanical properties, hot work or "hot processing" of the material above the recrystallization temperature must be possible and should be started with the basic ingot. In order to accomplish this with arc cast molybdenum (Mo), efficient controlled atmosphere furnaces capable of reaching and maintaining equilibrium temperatures of 3,500° F to 3,600° F are required. The best furnaces available will yield temperatures between 2,700° F and 2,900° F and the capacity of any such furnace is fairly small. In general, the higher capability furnaces are smaller, cylindrical, induction-heated apparatus and therefore are not very conducive to the processing of plate and sheet.

After the ingot is partially warm or hot-cold worked by extrusion and maybe by further swaging into sheet bar, the recrystallization temperature begins to lower. However, the problem of impurities still exists and now, in particular, oxidation and nitriding of the material may occur.

Mo does not exhibit a high degree of oxygen penetration since, at the temperatures under consideration, the oxide product (MoO_3) is volatile and, in processing, this problem could be overcome by either a good vacuum or a reducing atmosphere such as high-purity dry hydrogen. Cracked ammonia will severely nitride and embrittle Mo and commercially available argon contains sufficient amounts of impurities to be quite deleterious. With niobium (Nb), it is different in that the oxide product is both

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stable and porous and, therefore, oxygen will continue to penetrate. Here, either a good vacuum or high-purity inert atmosphere is required.

Now, when an attempt is made to roll the sheet bar into sheet, especially thinner gages, the aforementioned problems are magnified. There are essentially no facilities available with necessary atmospheric control. An exception to this statement is the Inert Fabrication (INFAB) facility at Universal Cyclops Steel which is sponsored by the Navy. This facility is a self-contained room with a minimum amount of necessary processing equipment which will be operated in an atmosphere of argon under slight pressure. At present, necessary, reliable, and adequate quality control is almost nonexistent. This is an area that needs very close attention; with it many of our problems, both present and future, can be alleviated or even eliminated.

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Consider joining for a moment. (See fig. 2.) It is generally conceded that Mo is very brittle and, therefore, susceptible to fracture in the cast state. This property makes welding a problem and so far no welds, either fusion or resistance, have been seen that did not exhibit severe grain growth and resultant brittle-type fractures. Nb is more amenable to welding, if in the pure state or even alloyed with certain elements. However, when the alloys which are most attractive for the reentry temperatures involved are considered, problems arise. On the USAF contract with McDonnell Aircraft Corporation the General Electric developed F48 alloy was chosen to fabricate the end item which is a fin and rudder with necessary hinge fittings and attachments but without a leading edge. As of today, it is highly questionable as to whether it is possible to weld it successfully either by fusion or resistance methods. It should be added, however, that at least one of the experiments conducted by the General Electric Company has shown promise in spot welding the F48 alloy. With a thin titanium foil (about 1 mil) inserted between the two sheets and by closely controlling the welding cycle, the notch sensitivity around the shoulder of the nugget has been noticeably reduced. Weld shear values have been increased and fractures are apparently less brittle.

Reasonable success has been realized in riveting both Mo and Nb. Marquardt Aircraft has been riveting and bolting Mo ramjet assemblies for some time but, in general, the detail parts were not coated prior to assembly. In fabricating the small test items under the McDonnell Aircraft Corporation contract, it was deemed necessary to multiple coat in some cases because of the configuration complexity. Figure 3 shows a W2 coated Mo$\frac{1}{2}$Ti rivet after squeezing. This condition meant using coated rivets, if possible, and this has been done. Even though it is still essentially a hand operation, Mo rivets can be manufactured easily, coated with a W2 or Durak MG type coating, and squeezed successfully by torch heating to 1,600° F or slightly above. Figure 4 shows some of the

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more easily manufactured fasteners other than rivets. Driving the rivets by impacting appears to be risky at present. Many other fastener configurations are being investigated and evaluated including blind-mechanical and explosive types. All the refractory metals which may be candidates for structural applications at present and in the foreseeable future are susceptible to oxidation, which can be catastrophic, at the temperatures involved. Molybdenum, which is under serious consideration, reacts violently with oxygen above 1,500° F to 1,600° F; therefore, it must be protected. So far, the only work or development in this area of any great import has been the cementation pack process which has produced a disilicide (or variation thereof) type of coating. This is the best of known available coatings for Mo. However, even though this may be suitable for short-time applications such as ramjet engines, it is not considered at this time to be uniform, entirely reproducible, or wholly reliable for long-time, multiple-mission structural applications. In static oxidation tests rather encouraging results have been realized at temperatures up to 2,500° F, but patching or repairing any kind of break or defect appears to be impossible.

The potential of Nb is somewhat more encouraging than Mo up to about 2,500° F, in that the oxide product is stable and not volatile and that Nb is inherently more oxidation-resistant than Mo but it still needs to be protected. However, if a coating failure occurs, the end product should not be as catastrophic as that with Mo. Figure 5 is a time-temperature static oxidation comparison between Nb and Mo alloys. From a relative viewpoint and under a given set of conditions, alloyed Nb can be 100 times as oxidation-resistant as Mo. Incidentally, so far, alloying Mo has not enhanced its oxidation resistance. Again, work on the McDonnell Aircraft Corporation - General Electric Company contract has proven a need for a Nb coating, and a fair amount of effort has been expended in this direction. At present, it appears that an aluminum base cold slurry dip, with subsequent heat treatment, may prove to be the best for this program which of necessity must be limited in scope of coating development.

At this point, it is appropriate to mention some more of the perverse characteristics of promising coatings for structural applications which could possibly offer us the needed protection. First, they are all brittle; at room temperature their impact value is essentially zero. Second, as a rule, their coefficient of expansion is very low, and, therefore, radically different and usually incompatible with the substrate. These two inherent characteristics generally cause, at one time or another, cracking, spalling, crazing, etc. The General Electric Company is investigating the possibility of a glass-like material for an overlay, on the Nb dip coating, which would become viscous at the temperatures under consideration and, thereby, fill and heal any cracks that may have developed.

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Production problems should be pointed out which have been encountered in procurement. An order can be placed for a lot of thin gage (below 0.020) material, having a given chemistry, exhibiting reasonable T bend and elongation characteristics at room temperature, and being free from scales, slivers, laminations, gouges, etc. With present technology, the chemistry requirements would probably be met except for a few undesirable segregations and possibly excessive amounts of contaminants. Thin-gage material has been ordered with a promised delivery of 8 weeks and 8 months later the complete order has not been received. Figure 6 is an ultrasonic trace recording of Mo sheet which has been fusion butt-welded. Notice the discontinuities in the weld zone and also the parent metal laminations. At present all material must be accepted on a best-efforts, consigned basis. This year material has been shipped as "supposedly acceptable" and, in the $\mathrm{Mo}\frac{1}{2}\mathrm{Zr}$, more than a half-dozen surface scales and slivers were evident in 1 square foot. Also, $\mathrm{Mo}\frac{1}{2}\mathrm{Ti}$ has been shipped as 0.010 gage in which the thickness varied from 0.0065 at one end to 0.0105 at the other in a 10-inch by 28-inch piece. This is not indicative of quality, quality control, reproducibility, or assurance that the material needed can be obtained today. However, as the gage thickness increases, problems decrease. For gage thicknesses of 0.050 up, either the $\mathrm{Mo}\frac{1}{2}\mathrm{Ti}$, $\mathrm{Mo}\frac{1}{2}\mathrm{Zr}$, or the TZM alloy could be made available in reasonable quantity and with reasonable quality, provided that necessary process control is exercised. Inspection techniques and/or establishment of acceptance standards and limits must still be optimized for these alloys.

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Another matter for consideration is expected or calculated yield. The program at McDonnell - General Electric was initiated with material basic cost being estimated at approximately $60 per pound for Mo sheet and $120 per pound for Nb sheet. First, with the more attractive alloys, such as the Nb base F48 and Mo base TZC, no more than a 10- to 20-percent yield from the ingot to thin-gage material has been realized. Second, if desired quality requirements were imposed, probably 90 percent of the yield would be rejected. Because of breakage, waste, rejections, etc., our original cost estimates have increased by factors of 5 for the thin-gage material and the material which is ultimately desired for fabrication into usable and reliable structures has not been obtained. Figure 7 does show that with careful processing techniques it is possible to hand fabricate small detailed parts.

CONCLUDING REMARKS

For structural applications other than heat shield and leading-edge elements, problems associated with ingot production, sheet quality control,

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available assembly, coating, and material cost have been presented. Because of these problems our confidence in structural applications of refractory materials is poor; however, it is hoped that, at the conclusion of the McDonnell - General Electric program in September, a satisfactory test of component hardware will be accomplished and the program will have indicated the steps which industry as well as the USAF must take to assure reliable efficient refractory structures. The creep and rupture properties shown in figure 8 are a very real reason why these refractory metals are so attractive for elevated-temperature structural and heat-shield applications.

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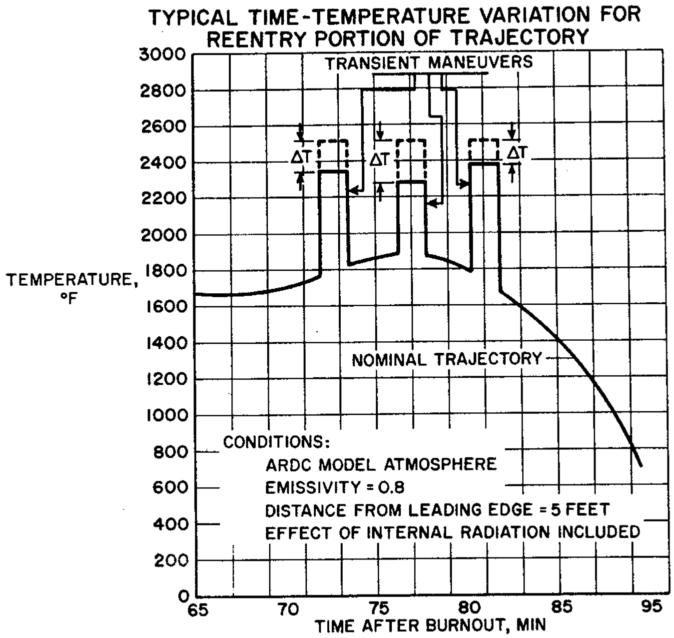

Figure 1

MOLYBDENUM ALLOY WELDING PROBLEMS

1. LOW DUCTILITY OF WELD DEPOSIT
    - a. LARGE GRAIN SIZE IN WELD AREA
    - b. CRATER CRACKING (OXYGEN)
    - c. GRAIN BOUNDARY CONSTITUENTS
2. POROSITY IN WELD DEPOSITS
3. ELECTRODE STICKING (RESISTANCE WELDING)
4. TENSILE PROPERTIES OF WELDS
5. POST WELD CRACKING (RESIDUAL STRESSES)

Figure 2

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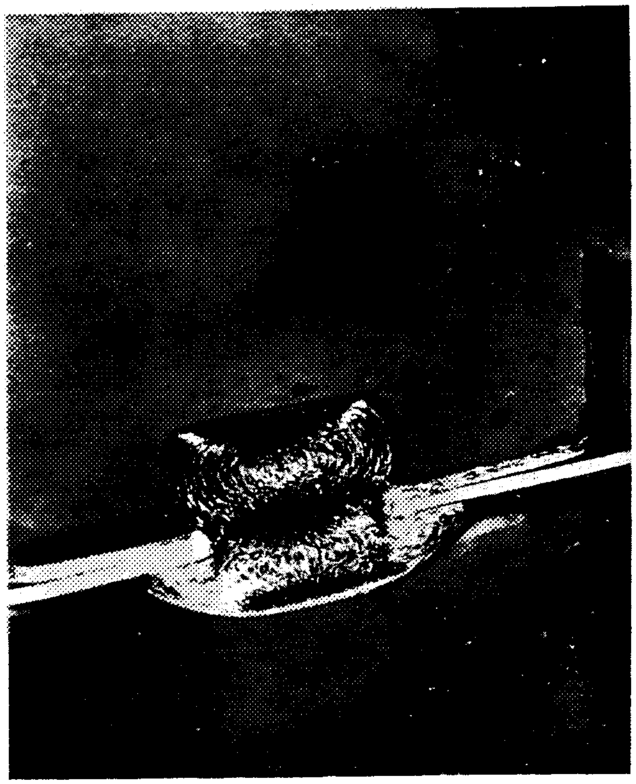

Figure 3

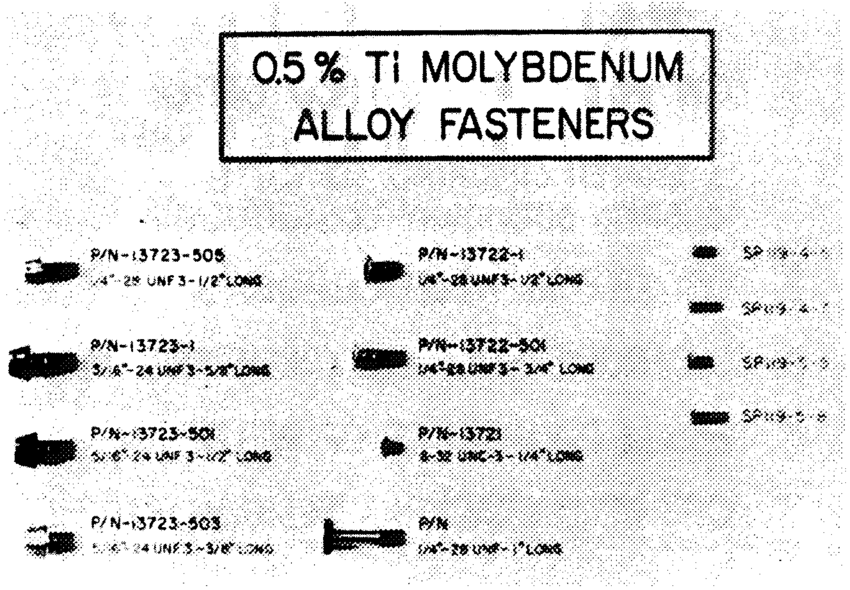

Figure 4

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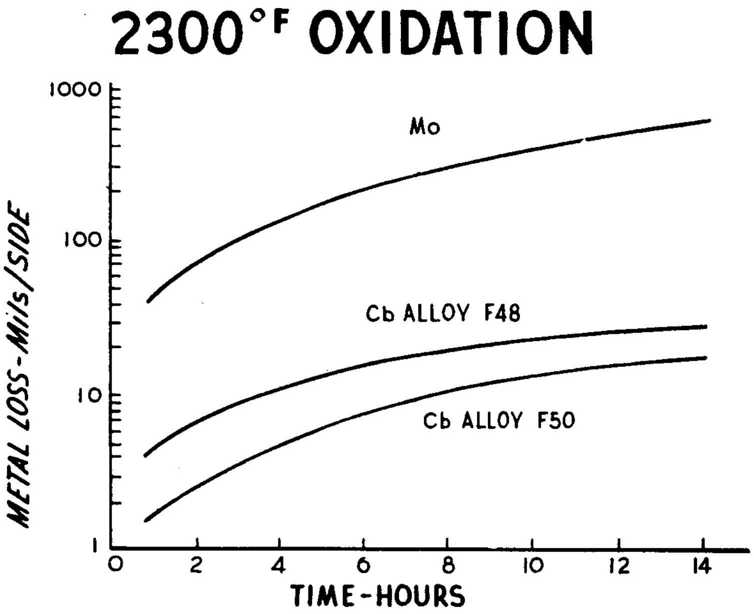

Figure 5

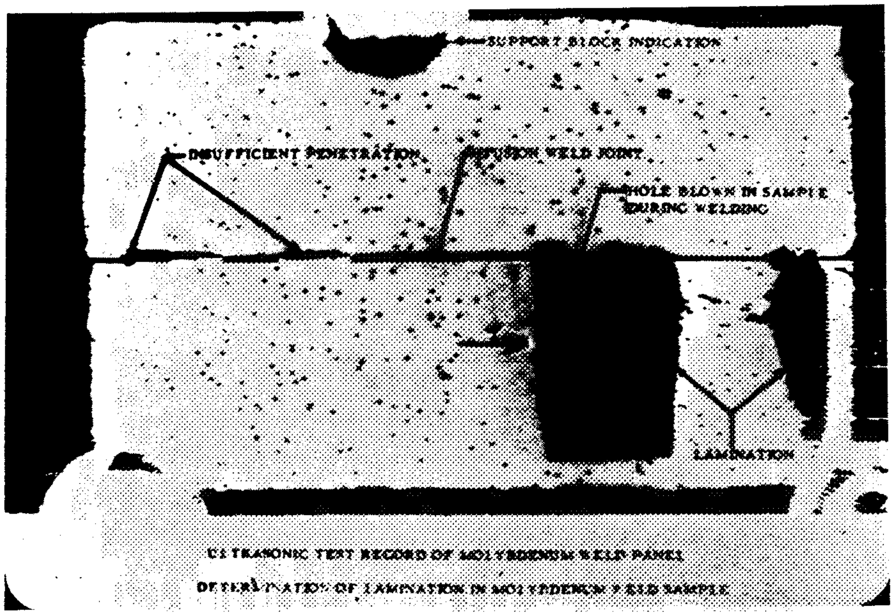

Figure 6

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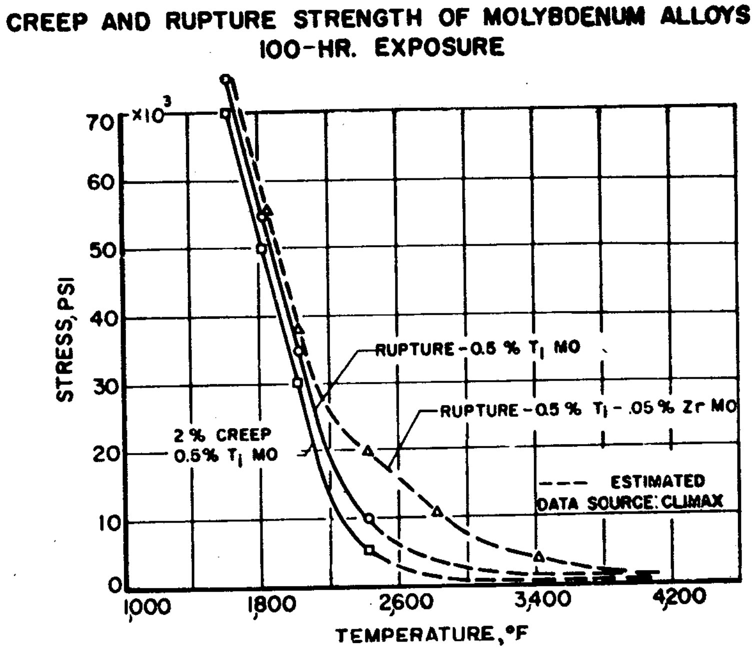

Figure 7

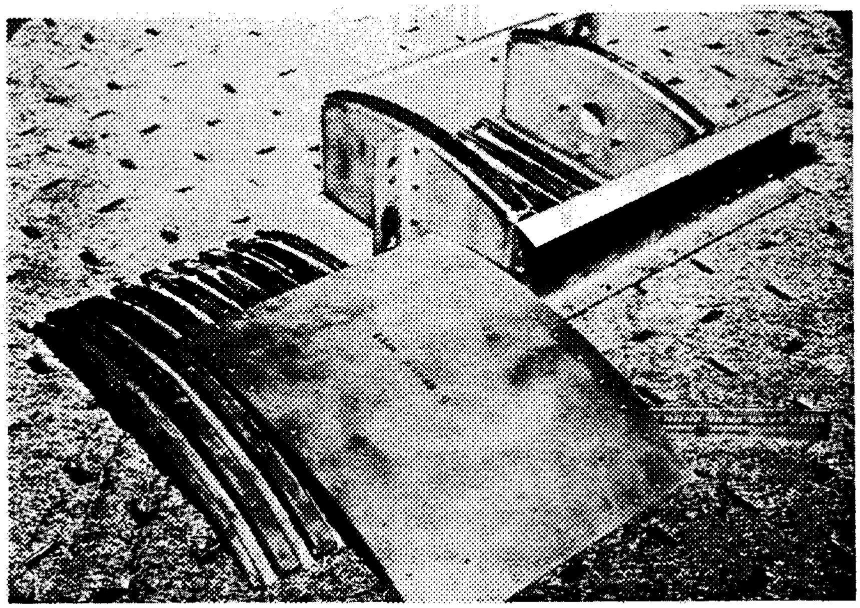

Figure 8

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