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"STRENGTHENING OF CHROMIUM-MAGNESIA COMPOSITES"

August 23, 1963

Department of the Navy, Bureau of Naval Weapons

Contract N600 (19) 59647 (C.P.F.F.)

Interim Report No. 3

Covering Period 1 June 1963 through 31 July 1963

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**BENDIX PRODUCTS AEROSPACE DIVISION
THE BENDIX CORPORATION
SOUTH BEND 20, INDIANA**

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Prepared By: G. C. Reed

ABSTRACT

This report describes the work accomplished during the third bimonthly period of a program ultimately aimed at strengthening chromium-ceramic composites. The initial effort has been directed toward optimizing ductility prior to investigating alloy additions for strengthening. In the previous reporting period, it was found that reducing the MgO content to 3% from the 6% level used in production chrome-30 material increased the tensile elongation almost twofold. Further studies of variations in MgO content are reported herein. These investigations have shown 2% MgO to be the optimum ceramic level from the standpoint of strength and ductility. The oxidation resistance of the composites containing various amounts of MgO was evaluated at 2200°F and appeared to be independent of the MgO contents studied. The tensile transition temperature of the extruded material containing 2% MgO was found to be approximately 35°F. The effects of annealing at 2500°F were also briefly investigated. A base composition for the alloy phase of the program was established as a result of these studies and fabrication of alloy extrusions has been initiated.

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1.0 INTRODUCTION

The overall plan for this program involves optimization of ductility in chromium-magnesia composites followed by an investigation of alloy strengthening. In the work reported previously, it was found that reducing the MgO content from the customary 6 weight % to 3% improved the tensile elongation significantly. It was then decided to pursue this approach with further studies of various MgO contents before proceeding with the alloying phase of the program. Most of the work accomplished during this reporting period consisted of evaluation of extrusions containing varying amounts of MgO in the neighborhood of the 3% level previously indicated as promising. The evaluations were expanded to include oxidation/nitridation studies. Impact testing was not included due to the non-definitive results obtained earlier in spite of closely controlled test conditions.

The work described in this report was carried out during the period June 1, 1963-July 31, 1963.

2.0 EVALUATION OF EXTRUSIONS AIMED AT IMPROVING DUCTILITY

2.1 Composition and Process Variables Investigated:

2.1.1 Four variations in MgO content (1, 2, 4, & 5 weight % respectively - balance Cr) were studied on the basis of the significant improvement in ductility exhibited previously by the experimental extrusion containing 3% MgO.

2.1.2 An extrusion made earlier in the program with BeO substituted for MgO was evaluated during this reporting period. A BeO addition of 2.5 weight % was chosen since it simulated the same volume percentage (5.86) as the 3 weight % MgO shown earlier to be promising. It was hoped that the BeO would offer more resistance to coalescence at elevated temperatures than MgO. BeO is also a spinel former like MgO and was, therefore, expected to produce the beneficial effects previously associated with the formation of the magnesio chromite spinel.

2.1.3 The effect on tensile properties of increasing the post-machining annealing temperature from 1800°F to 2500°F was evaluated for two of the experimental composites included in this investigation.

2.2 Extrusion Procedures:

2.2.1 The four MgO variation billets included in this study were extruded at the ASD Metals and Ceramics Laboratory at Wright-Patterson AFB, Ohio. All extrusions were processed successfully. The billets were flame sprayed with a .030" thick nickel coating. They were extruded at 2200°F using a ratio of approximately 10:1.

Corning 0010 borosilicate glass was used for lubrication. The extrusions were in the form of flat bars roughly 0.4" thick by 1.8" wide.

2.2.2 The extrusion containing BeO was extruded by Nuclear Metals, Inc. Handling problems related to the toxicity of BeO necessitated the change in extrusion facilities. This billet was canned in mild steel. It was extruded at 2200°F at a ratio of 10:1 into the form of round bars approximately 1" in diameter.

2.3 Chemical Analyses:

2.3.1 Samples of each of the five extrusions described above were analyzed by Ledoux and Company of Teaneck, New Jersey. The reported impurity levels are summarized in the Appendix (Section 5.1). The results show considerable scatter and fail to reveal any positive relationships with additive content. The nitrogen level was found to be quite high in the extrusion containing BeO, however. This may explain the poor tensile properties exhibited by this material.

2.4 Microstructures:

2.4.1 Microsections were prepared for each sintered billet and each extrusion. The microstructures representing the as-sintered billets containing various amounts of MgO revealed considerable porosity but uniform ceramic dispersion. The as-sintered specimens containing BeO exhibited very poor distribution of the BeO which was concentrated in fairly large clumps. The extruded microstructures of the MgO variations revealed good ceramic dispersion in a dense matrix of clean chromium grains. The variations in MgO content resulted in little difference, if any, in the chromium grain size. Microcracks were noted in all of these extruded sections but it is not known whether they occurred during extrusion or as a result of mishandling during mounting and preparation of the microsections. The good tensile properties exhibited by these materials would indicate that the latter was the case. The extruded structure of the BeO composite reflected the poor ceramic dispersion seen in the as-sintered material. The longitudinal section of this extrusion revealed segregated stringers of BeO surrounded by a rather dirty chromium matrix.

2.5 Sintered and Extruded Densities:

2.5.1 The densities of each of the sintered billets and extrusions involved in this reporting period are tabulated in the Appendix (Section 5.2). The as-sintered billet densities were determined by weighing each machined billet and calculating its volume from dimensional measurements. The densities for the extrusions were determined with small representative specimens using the Archimedes method. These specimens were taken near the lead-

ing end of each extrusion. It will be noted that the average extruded density for these materials is well over 98% theoretical.

2.6 Tensile Testing:

2.6.1 Tensile Properties vs. MgO Content: Three unnotched tensile specimens were prepared from each extrusion. A modified ASTM bar with a 3/4" gage length and a reduced section diameter of 0.189" was used. The reduced section of each bar was polished by hand with emery paper to a finish of less than 20 rms. Electro-polishing was not employed. A snap-on extensometer was used to record elongation during the test. The MAB standard procedure for refractory metals, No. 176-M, was followed. This calls for a strain rate of 0.005 in/in/min in the elastic region and 0.05 in/in/min in the plastic region. All tests were performed at room temperature. The results of these tests are plotted in the Appendix (Section 5.3) along with previous data obtained earlier in this program from other extrusions containing MgO variations. It will be noted that there is remarkably little change in strength and elongation in the range from 1-6% MgO although a decrease in both properties was observed at the 9% MgO level. All material containing MgO, even at the 1% level, exhibited significantly better tensile properties than pure Cr specimens fabricated in an identical manner. The peak elongation values were obtained with the material containing 2% MgO. In accordance with previously established procedures, all of these test specimens were heat treated for 1 hour @ 1800°F prior to testing to relieve surface stresses resulting from the machining operations.

2.6.2 Tensile Transition of Cr + 2% MgO: Several more tensile specimens were prepared from the Cr + 2% MgO extrusion following the procedures described in 2.6.1. These bars were tested at several temperatures from 0°F to 75°F in an attempt to establish the tensile ductile-to-brittle transition temperature. Alcohol and dry ice mixtures were used to attain the lower test temperatures. The data is plotted in the Appendix (Section 5.4). Although the number of tests run was admittedly rather limited, they were sufficient to indicate a tensile ductile-to-brittle transition temperature in the neighborhood of 35°F. The low and coincident yield and ultimate strength values observed at 0°F and 20°F are probably indicative of premature failure rather than true strengths.

2.6.3 Effect of High Temperature Anneal on Tensile Properties: At the request of the contracting agency, a brief survey was made to determine the effect of a 2500°F annealing cycle (rather than the customary 1800°F) on the tensile properties of chromium composites. Tensile specimens were prepared from several materials as described previously. After polishing, some were heated in H₂ for 1 hour @ 2500°F and some were given a similar treatment in vacuum. Slight roughening of the surfaces was noted in both cases

due to chromium evaporation. The tensile properties of these specimens was erratic. The Cr + 3% MgO material, for example, gave elongation values ranging from 2.5 to 25% and ultimate strengths from 29,000 to 47,000 psi when tested at room temperature following the 2500°F anneal. Next, three samples of extruded bar stock of the Cr + 2% MgO material were given a flame sprayed coating of ZrO₂ (to eliminate evaporation losses) and heated for 1 hour @ 2500°F in vacuum. These pieces were then machined into tensile specimens, given a post-machining heat treatment of 1 hour @ 1800°F in vacuum (to relieve machining stresses) and tested at room temperature. The results from these tests were favorable. The average ultimate strength (47,000 psi) and elongation (44%) in these three tests were in the range exhibited by similar material heated at 1800°F only. Thus, the 2500°F heat treatment does not appear to be detrimental if the effect of surface irregularities is eliminated.

2.6.4 Tensile Properties of Extruded Cr + 2.5% BeO: This composite was described in Section 2.1. Machining tensile specimens from this extrusion was difficult and the resulting test bars had numerous surface defects. This was undoubtedly due to the poor microstructure and high impurity levels discussed previously. Of the six room temperature tensile tests conducted with this material, five specimens broke outside the reduced section. The highest ultimate strength and elongation values obtained were 47,500 psi and 1.95% respectively. In view of these results, no further evaluation is planned for this material.

2.7 Oxidation/Nitridation Studies:

2.7.1 Techniques for evaluating the resistance of material systems to oxidation and nitridation should be chosen to supply information most valuable to the designer or user. Obviously, different applications will require different types of data. A three fold approach was selected for this program. First, conventional thermogravimetric or weight gain vs. time studies were made for 10 hours @ 2200°F in dry air flowing at 1 cfh. Since the surface oxide-complex layers tended to scale off the test samples upon cooling, a second evaluation was to determine the amount of material consumed by oxide formation. This was done by measuring the sample thickness before exposure and again after the test with the surface scale removed. A third evaluation consisted of determining the depth of nitride penetration microscopically using polished sections of the same test specimens.

2.7.2 The weight gain vs. time data for several extruded composites containing various amounts of MgO is presented in the Appendix (Section 5.5). Three samples of each material were tested. The data indicates that the variation in results obtained for different materials is no greater than the variation between like samples. This is somewhat inconsistent with the results of in-

vestigations run prior to this program in which materials containing MgO were far superior to pure Cr and did not exhibit this lack of reproducibility at 2200°F. The previous studies indicated that parabolic, diffusion-controlled oxidation resistance in air wasn't lost until exposure temperatures reached approximately 2400°F. Recently, modifications have been made to improve the accuracy and control of the thermogravimetric apparatus used in these studies. In light of the results reported herein, it can be concluded that the critical temperature from the standpoint of oxidation resistance is at 2200°F or below. Further tests should be run at 2000°F on a selected group of samples to verify these findings.

2.7.3 The thickness change measurements aimed at determining the material loss involved in oxide scale formation were inconclusive. In all cases, the total thickness loss was less than 0.0005" and was considered immeasurable. Although no differences could be attributed to variations in MgO content, the actual loss in sound substrate material was shown to be insignificant for the test exposure of 10 hours @ 2200°F.

2.7.4 The polished sections of the test samples being made for nitride penetration determinations are still in preparation. Preliminary examinations indicate little difference, if any, in the penetration observed in the various materials. The nitrogen-rich surface layers are easily distinguished microscopically and appear to vary in depth from approximately .001" to .002" on each sample.

3.0 SELECTION OF ALLOYING PARAMETERS FOR STRENGTHENING STUDY

The tensile data obtained to date have shown that magnesia additions at the 2 weight % level are most beneficial from the standpoint of optimizing ductility without sacrificing strength. The oxidation/nitridation studies have shown that there is room for improvement in this area. Since the evaluation of various methods for improving oxidation/nitridation resistance is beyond the scope of this program, it was decided to take advantage of published work in this area. This approach also avoids duplicating the efforts of others. The literature reveals that several investigators have found small additions of yttrium to be very helpful in improving the oxidation of chromium. Since additions of 1 weight % and greater are reported to result in hot shortness, smaller additions are preferable. Consequently, it was decided to incorporate 0.5 weight % yttrium in the base composition for the alloy study planned for this program. The base composition selected consists, then, of 2.0 weight % MgO, 0.5 weight % Y, and the balance Cr. In view of the emphasis on ductility improvement agreed to midway in this program and the limited time remaining, the number of alloying additions to be studied had to be necessarily curtailed. On the basis of homogenization studies and

other preliminary investigations, columbium additions of 1, 2, and 3.5 weight % were selected as the most promising for producing solid solution strengthening. Four extrusion billets are now being processed representing the base composition and the three additions selected. These will be extruded and evaluated during the final bimonthly experimental period of this contract.

4.0 FUTURE PLANNING

4.1 The Following Work is Planned for the Final Phase of This Program:

- 4.1.1 Preparation and extrusion of four billets representing the compositions selected for the alloying study.
- 4.1.2 Determination of densities and hardnesses of each of these four extrusions.
- 4.1.3 Preparation of microsections of each extrusion.
- 4.1.4 Determination of impurity and additive content of each material after extrusion.
- 4.1.5 Evaluation of short-time room and elevated temperature un-notched tensile properties of each extrusion up to 2400°F.
- 4.1.6 Evaluation of oxidation/nitridation resistance of each extrusion including behavior exhibited under conditions involving cyclical exposure above 2000°F.
- 4.1.7 Preparation of final report.

5.0 APPENDIX

(These items are found on the following pages)

- 5.1 Chemical Analyses of Recent Extrusions.
- 5.2 Composite Densities: As-Sintered and After Extrusion.
- 5.3 Plot of Tensile Properties vs. MgO Content.
- 5.4 Plot of Tensile Transition Data For Cr + 2% MgO Extrusion.
- 5.5 Plot of Weight Gain vs. Exposure Time in Air @ 2200°F for Various Extruded Composites.
- 5.6 Distribution List.

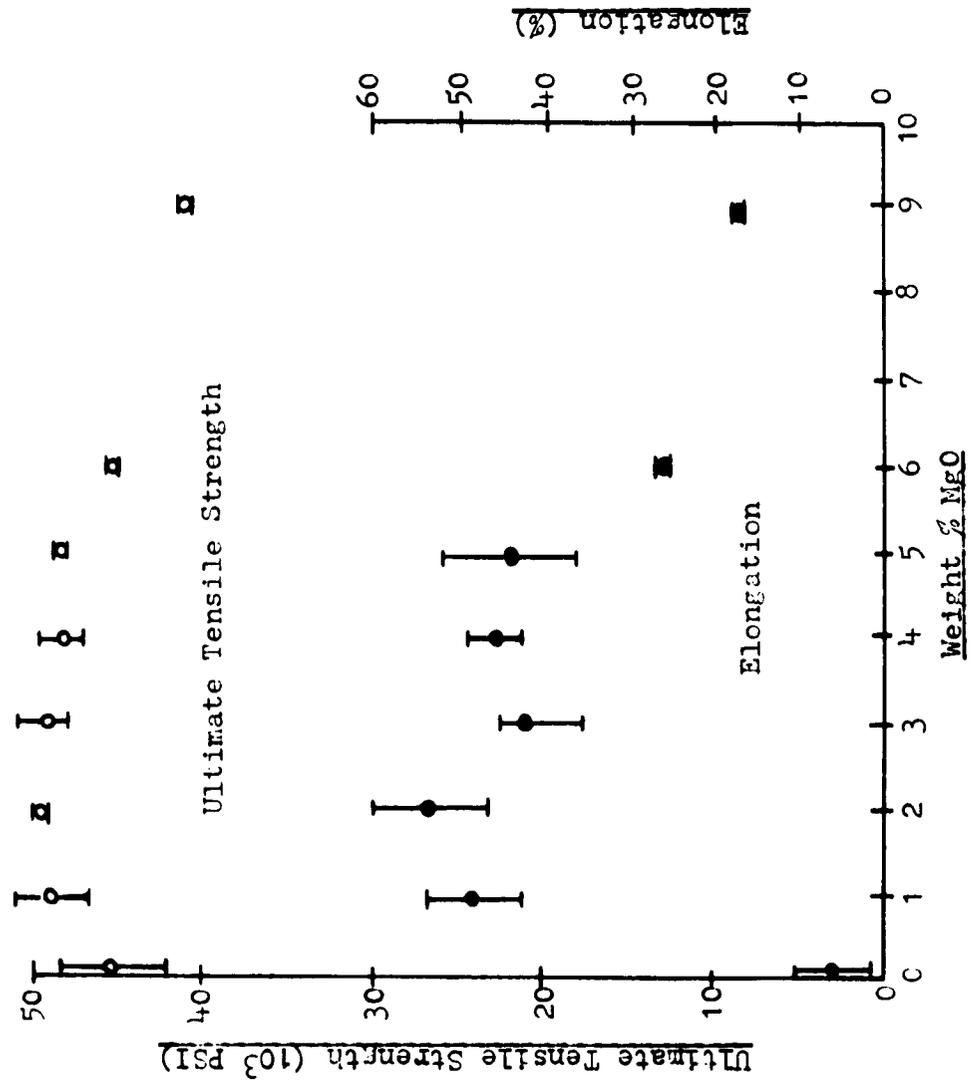
<u>Compound Code Number</u>	<u>Nominal Composition (Weight %)</u>	<u>Elements Reported</u>				
		<u>C (ppm)</u>	<u>N (ppm)</u>	<u>S (ppm)</u>	<u>Mg (%)</u>	<u>Be (%)</u>
223.578EA118	Cr + 1% MgO	55	58	215	0.30	-
224.577EA117	Cr + 2% MgO	44	99	132	0.62	-
225.576EA116	Cr + 4% MgO	223	46	75	1.67	-
226.575EA115	Cr + 5% MgO	111	126	135	2.24	-
196.565EN1	Cr + 2.5% BeO	148	591	159	-	0.91

5.1 Chemical Analyses of Recent Extrusions

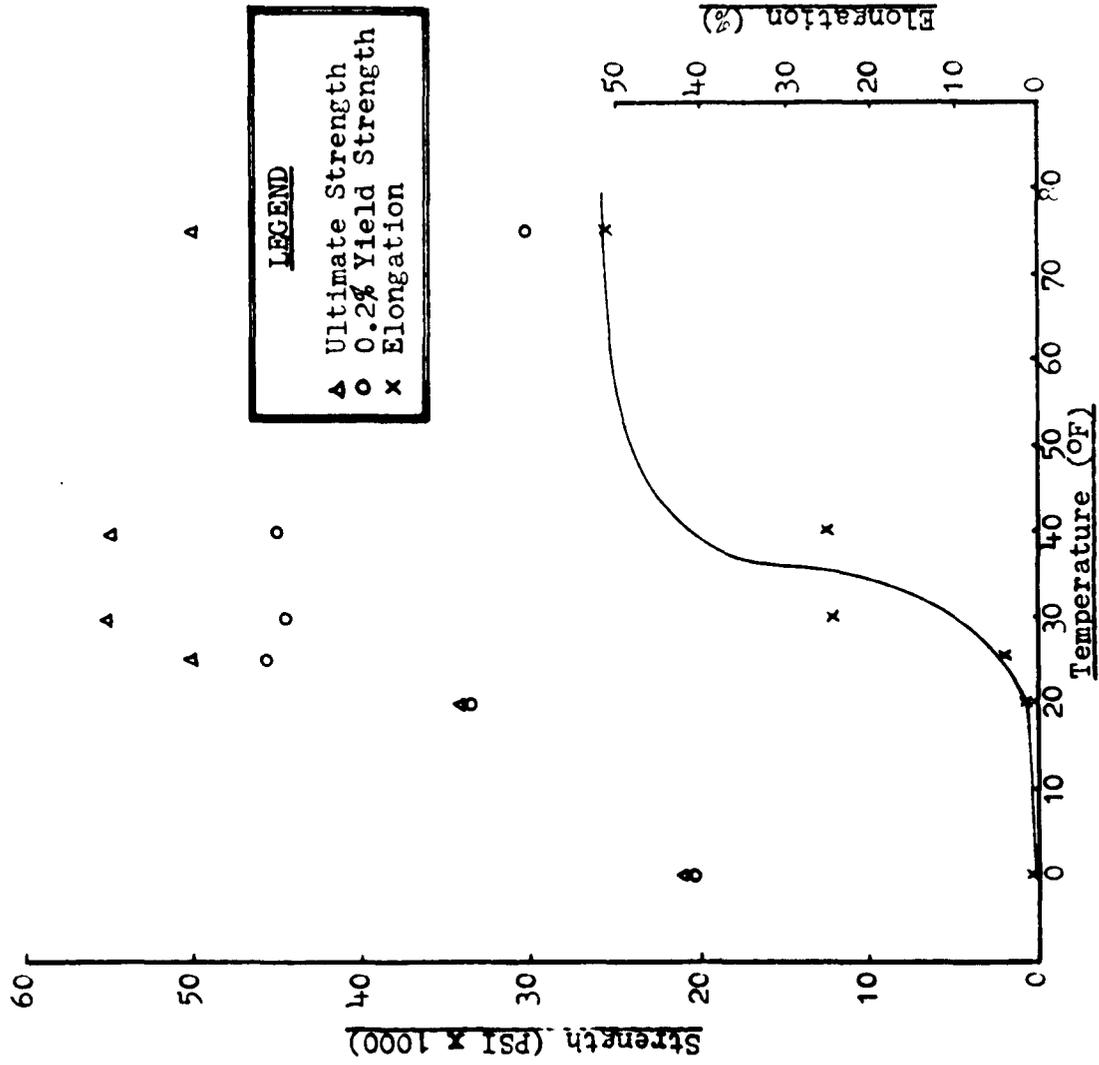
<u>Compound Code</u>	<u>Nominal Weight % Composition</u>	<u>Sintered Density gm/cc</u>	<u>% Theoretical</u>	<u>Extruded Density gm/cc</u>	<u>% Theoretical</u>
2400-223	Cr + 1% MgO	5.35	75.0%	7.03	98.5%
2400-224	Cr + 2% MgO	5.34	75.6%	6.94	98.4%
2400-225	Cr + 4% MgO	5.40	78.0%	6.87	99.4%
2400-226	Cr + 5% MgO	5.36	78.3%	6.79	99.1%
2400-196	Cr + 2.5% BeO	5.28	75.8%	6.82	97.9%

∞

5.2 Composite Densities: As-Sintered and After Extrusion

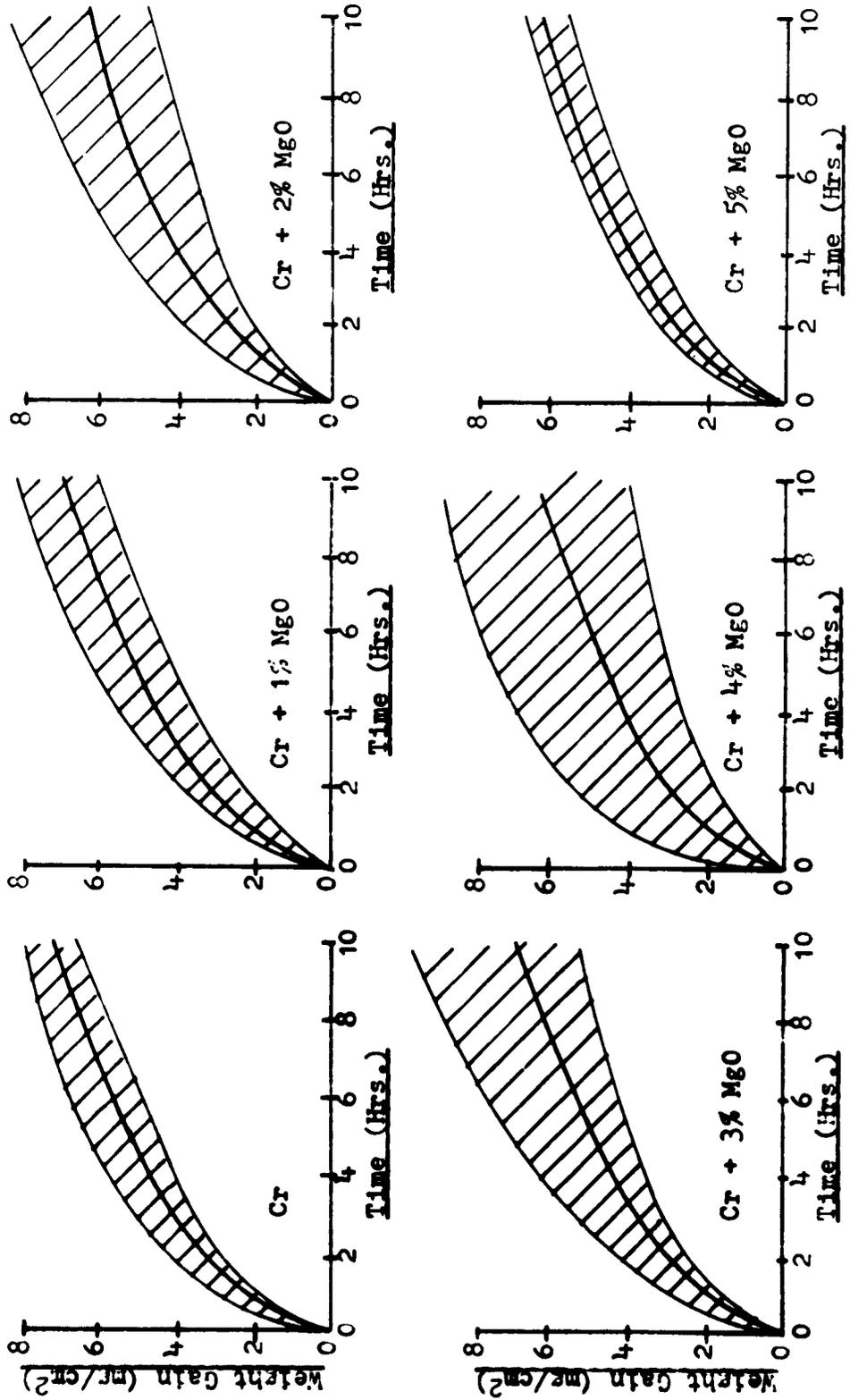


5.3 Plot of Tensile Properties vs. MgO Content



5.4 Ductile-To-Brittle Transition Study of Extruded Cr + 2% MgO

Note: Solid lines show average values for the three tests run with each material & cross-hatched regions show maximum variation in values.



5.5 Plot of Weight Gain vs. Exposure Time in Air @ 2200°F for Various Extruded Composites

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