ASD 8-170 (IV)

AMC INTERIM REPORT 8-170 (IV)
July, 1964

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HOT WORKING EVALUATION OF REFRACTORY AND REACTIVE METALS

Contract AF 33(657)-11270

Fourth Interim Report

1 April 1964 to 30 June 1964

Prepared By

John Bonchak

UNIVERSAL-CYCLOPS STEEL CORPORATION
REFRACTOMET DIVISION
BRIDGEVILLE, PENNSYLVANIA

The tendency of refractory and reactive metals to be contaminated in the InFab argon atmosphere was investigated. The results of exposures for various times, temperatures, and argon purity levels were evaluated by microhardness traverses, metallographic examination, chemical analyses and bend tests. With due consideration to extraneous variables and accuracy of the test methods, the results have been appraised.

METALLURGICAL PROCESSING BRANCH
MANUFACTURING TECHNOLOGY LABORATORY
Wright-Patterson Air Force Base, Ohio

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FOREWORD

This Interim Technical Progress Report covers the work performed under Contract AF33(657)-11270 from 1 April 1964 to 30 June 1964. It is published for technical information only and does not necessarily represent the recommendations, conclusions or approval of the Air Force.

This contract with the Refractomet Division, Universal-Cyclops Steel Corporation, Bridgeville, Pennsylvania, was initiated under AMC Aeronautical Systems Center, Project 8-170, "Hot Working Evaluation of Refractory and Reactive Metals." It is administered under the direction of Mr. Hugh L. Black, Project Engineer, Metallurgical Processing Branch, Manufacturing Technology Laboratory, AMC Aeronautical Systems Center, Wright-Patterson Air Force Base, Dayton, Ohio.

Mr. John Bonchak is the Project Engineer in charge. W. J. McElhaney, InFab Engineer, contributed significantly to the program.

Since the nature of this work is of interest to many fields of endeavor, your comments concerning the program are solicited.

****

PUBLICATION REVIEW

Approved By L. M. Bianchi

L. M. Bianchi
Technical Manager
Refractomet Division

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I. Introduction

The Purpose of this program is to improve the State-of-the-Art of processing refractory and reactive metals. Its objective is to explore the feasibility and advantages of hot-work processing these metals in an argon atmosphere.

The investigations are to encompass:

1. An evaluation of the ability of argon atmosphere to prevent contamination of representative refractory metals exposed to various conditions of time, temperature and work.
2. A direct comparison of the quality and properties obtained on refractory alloys processed InFab with those obtained on the same material processed by conventional methods.

II. Program

To accomplish its objective the program has been established to constitute the following four phases, some of which are carried out simultaneously.

Phase I	Investigation and Evaluation of Contamination
Phase II	Further InFab Process Development
Phase III	Process Development Without Protective Atmosphere
Phase IV	Comparative Metallurgical and Mechanical Property Evaluation

In the previous report covering the period 1 January 1964 to 31 March 1964, microhardness and bend test data along with photomicrographs for most of the exposure samples were presented and dicussed. From a comparison between the various test results it became evident that additional tests would be required to obviate those results which could be hinged to extraneous factors and to substantiate those which were not.

The additional test results presented in this report along with the results reported earlier have been analyzed. The deductions reached were founded upon observations within the recognized limits of test accuracies and held to the metallurgical definement of contamination.

A. Definitions

To maintain some clarity in ensuing discussions, contamination shall be defined as the defilement of metal properties resulting from adsorption of foreign elements. It becomes apparent from this definition that "defilement of metal properties", the "degree of contamination" and "the extent of contamination" become relative terms dependent on the property changes being measured and the precision of the measuring methods employed. Henceforth, for this investigation the "degree of contamination" shall be defined as the concentration of foreign elements producing a definable degree of change in the metal properties or interstitial content. The extent of contamination" shall be defined as the depth to which foreign elements are present of such quantity as to effect an observable change in the metal properties. "The defilement of properties" shall be related to contamination only when the test results are not obscured by extraneous conditions which also have a strong influence on the property being measured.

B. Methods for Measuring Contamination

The methods for measurement of contamination used in this investigation were hardness traverses, microstructure studies, chemical analyses, bend tests and weight gain measurements. None of these measurements have absolute accuracy and/or dependence only upon contamination; for discriminating results therefore the method's accuracy and dependence on contamination must be considered in analyzing the data.

Microhardness traverse results could be considered meaningful only when the degree or extent of contamination are of such magnitude that the influence of microstructural or stress-strain conditions would be negligible. This can be an expedient method for determining possible contamination of heat treated material. The criterion, however, is the measured hardness increase on a test specimen known not to have been contaminated prior to treatment and already in the annealed condition.

Bend test results before and after removals of surface layers can provide a general comparison between the effects of different exposure atmospheres for a given time-temperature treatment. Again reservations have to be made for such influencing factors as microstructures, stress-strain variations and surface quality or texture of the sample. It should be recognized that improvements after surface removals can be attributed not only to the removal of possible contamination but also the other factors such as improved surface quality and the slight increase in the bend radius.

Microstructural examination can be an expedient means for detecting and measuring contamination but only under certain conditions. Contaminants within the solid-solubility limits will not be revealed although their concentration may be at a level which would significantly affect the properties of concern. Proper sample preparation may be a pre-requisite for detecting contamination even if it is beyond the stage of solid-solubility. Material possessing a worked structure would require an annealing treatment which would bring about a preferential recrystallization hence distinction between the contaminated and uncontaminated zones. However, unless rigid precautionary measures are taken, such anneals may themselves produce or add contamination.

Since it is not subject to metallurgical conditions, chemical analysis is generally considered the most exact method for

determining the extent or degree of contamination. By successively obtaining analyses after progressive surface removals the content of each removed surface layer can be determined by simple calculation. However, this method would require numerous check analyses to ascertain accuracy within the desired limits. A difference of 10 ppm in the average analysis after a surface removal can result in several hundred ppm calculated for the removed surface layer.

Weight gain measurements also not subject to microstructural or surface conditions can be affected by human error on occlusion of foreign matter.

III. Evaluation of Time-Temperature Exposure Samples

A. Cb Exposures

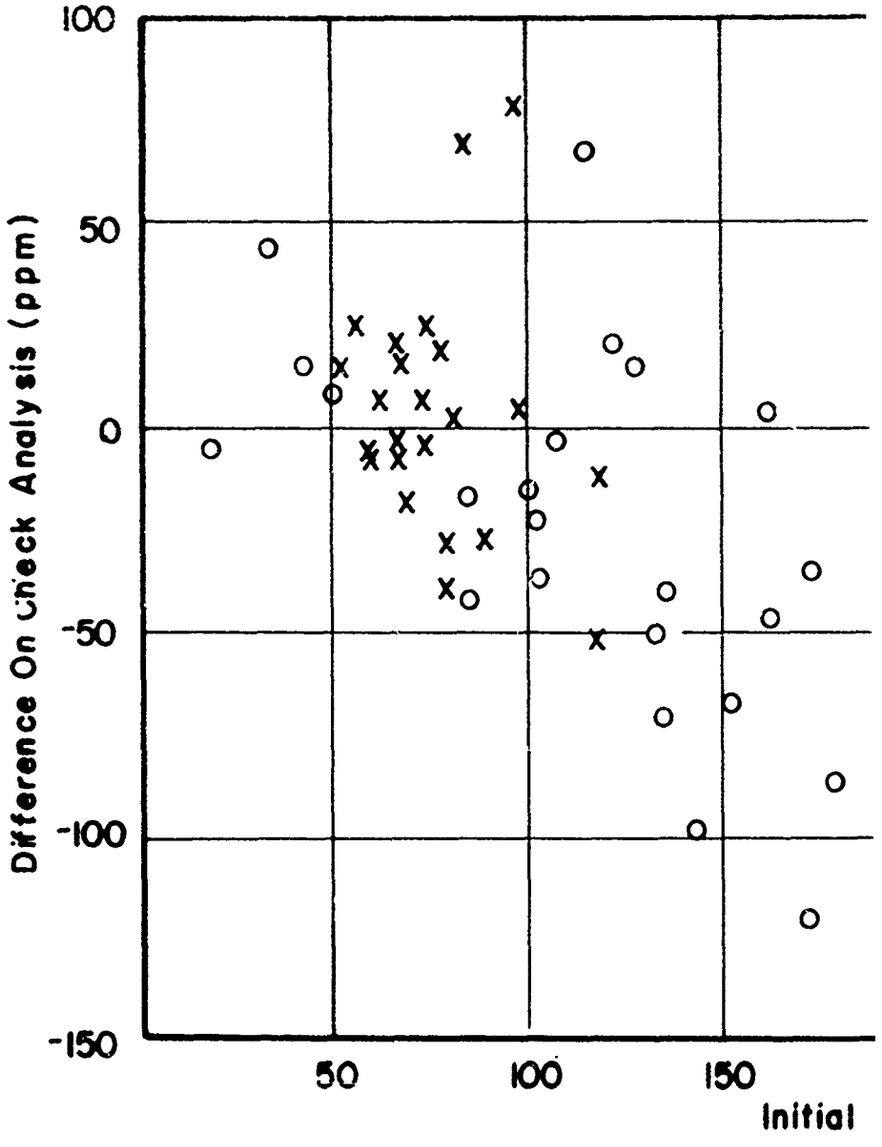
In the previous report it was shown by photomicrographs that no evidence of contamination was revealed by microstructural examination. From these examinations it was assumed that the pickup of atmosphere contaminants did not proceed beyond the solid-solubility limit.

The results of microhardness traverses did not show differences between the center and near-surface readings which would indicate a contaminated layer. The greatest spread in readings (70 KHN) was observed in a sample exposed for 1 hour at 2000°F. This spread was between the lowest reading and a single high reading which was not duplicated at an equal distance from the opposite face of the strip sample. The spread for the opposite face, and for another strip given the same exposure of time and temperature was no higher than 47 KHN. No correlation could be made between the hardness values and the results obtained by bend tests or chemical analysis. A strip sample, which exhibited a greater spread in hardness than its time-temperature counterpart of another series, was exposed to a higher purity atmosphere and showed less pickup of contaminants. Strip samples exposed for

1 hour at 3000°F showed greater pickup of interstitials than the 2000°F exposure samples yet exhibited a hardness spread of no more than 11 KHN. Since all of the samples exposed for 1 hour at 2000°F were successfully bent to a O-T bend radius and 105° bend angle at -320°F regardless of differences in hardness, it was assumed that the hardness values discriminated only between microstructural and stress-strain variations.

While the order of magnitude of analytical results appeared logical for the various exposure conditions, the accuracy became questionable when oxygen contents for 11 of 24 samples and nitrogen for 13 of the 24 samples were reported higher after surface removals of 2 mils per face. Check analyses of these samples not only failed to improve this situation but further demonstrated inaccuracies in the results. Figures 1 and 2 illustrate the divergence of check analysis results from the initially reported results for O_2 and N_2. Note in some instances (Figure 1) check results were higher than initial results while in other instances they were lower.

In an effort to expound this situation 14 samples, 7 from each of two exposure strips, were analyzed for oxygen by a second laboratory selected by Wright Field. The results reported by the second laboratory are shown in Table I with the results reported by the first laboratory for the same exposure strips. The spread of values reported by the second laboratory and the deviations from the averages of these values were also plotted on the graphs shown as Figures 1 and 2. From these graphs it was apparent that the accuracy of the second laboratory was no better than that of the first laboratory. It may be of interest to note that one laboratory uses the inert gas fusion method for oxygen determinations while the other used the vacuum fusion method.



FIG

RESULTS OF ANALYTICAL REC

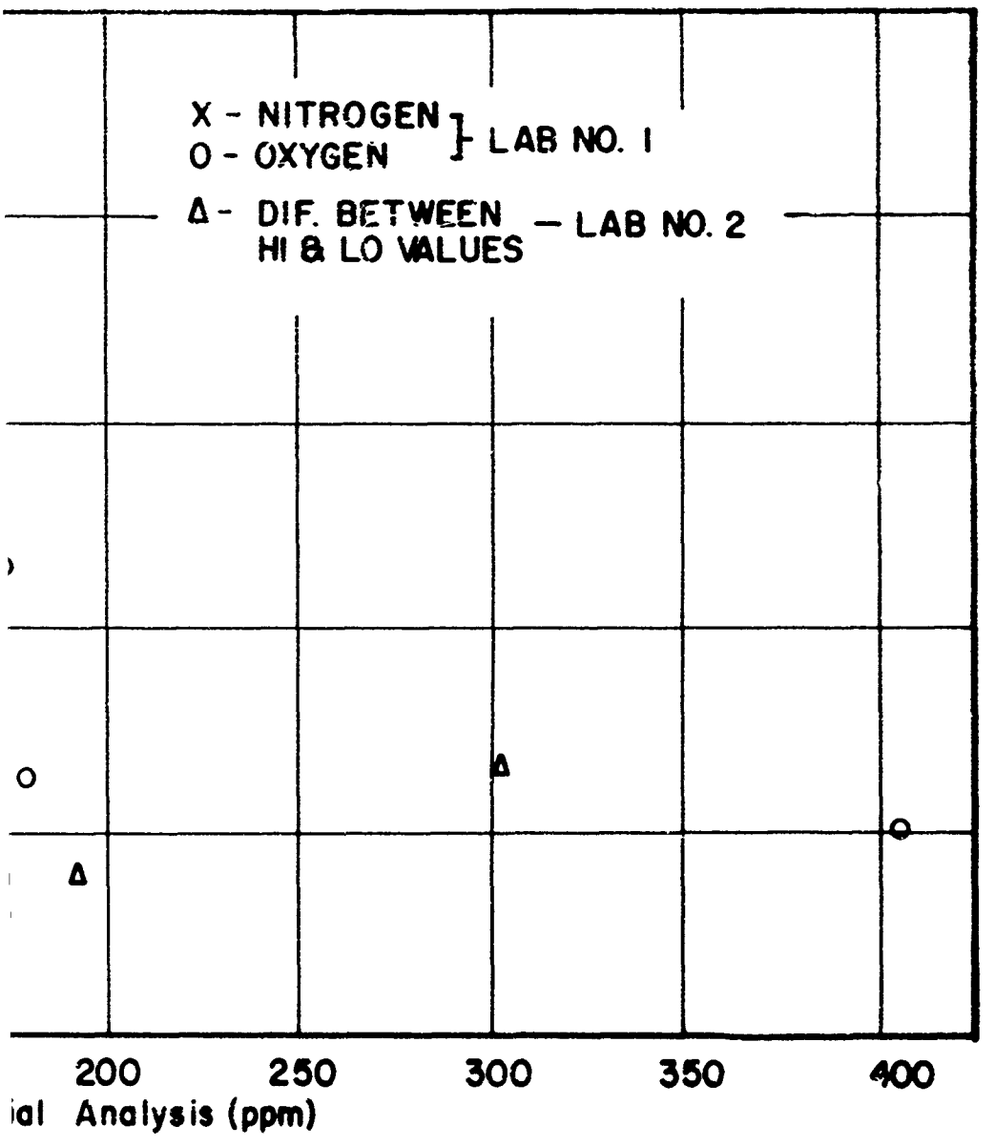


FIGURE 1

RECHECKS ON COLUMBIUM SAMPLES

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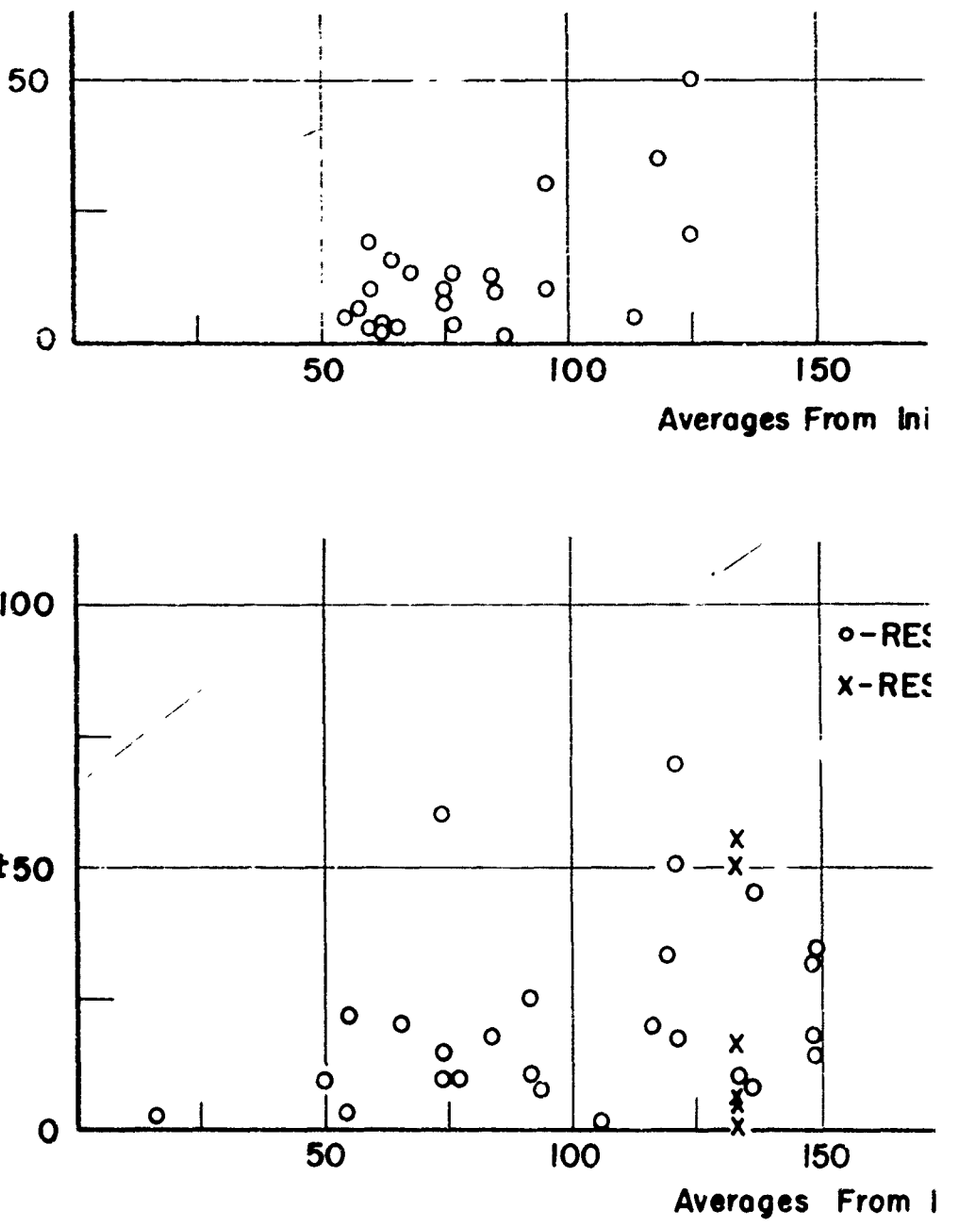
5/5/64



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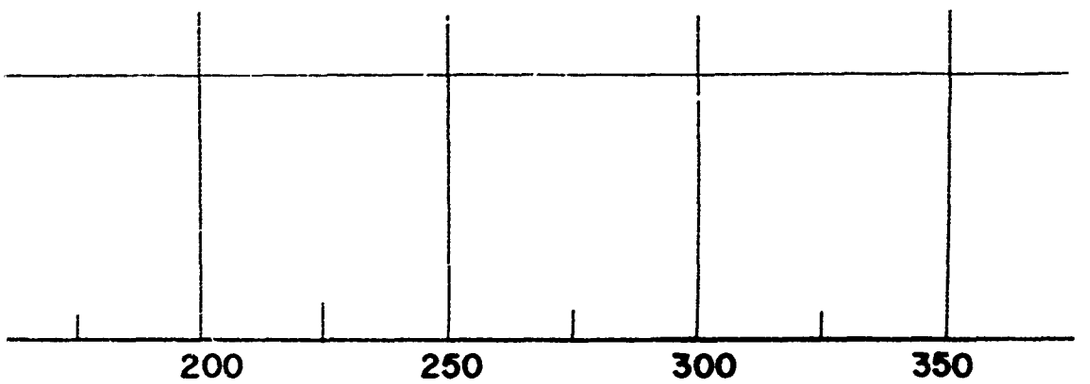
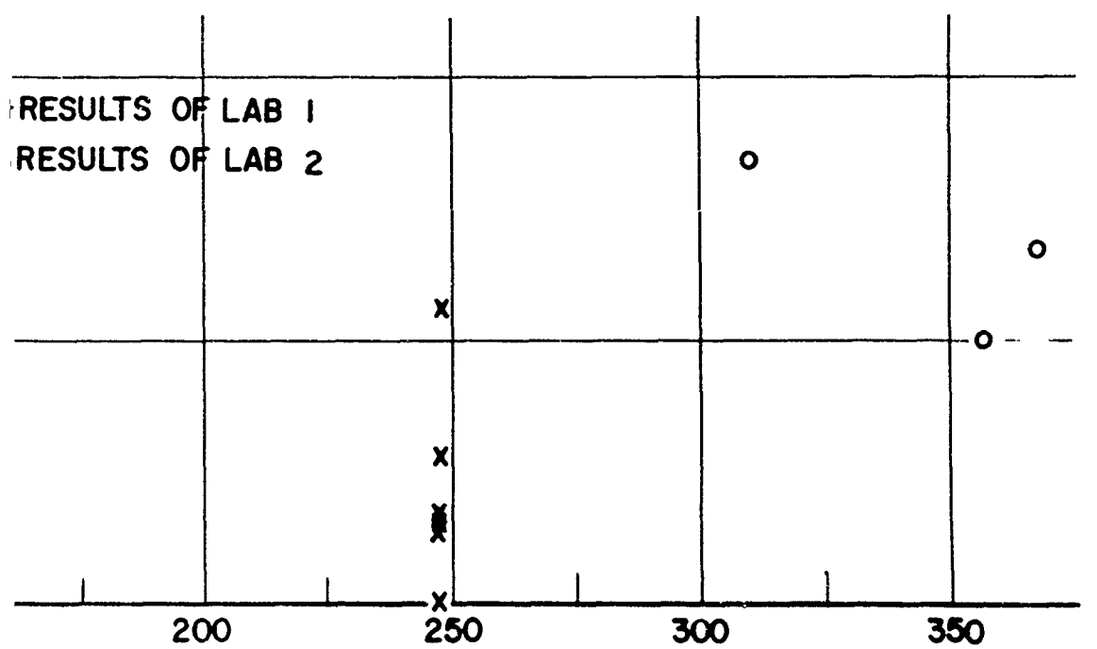
DEVIATIONS FROM AVERAGES
FOR O_2 AND N_2 IN COLUMB



Initial & Check Analyses – N_2



m Initial & Check Analyses – O_2

FIGURE 2

ES OF INITIAL AND CHECK ANALYSES
MBIUM SAMPLES

TABLE I

OXYGEN DETERMINATIONS ON INFAB EXPOSED Cb SAMPLES
AS REPORTED BY TWO TEST LABORATORIES

Test Laboratory No. 1 Results

Sample No.	O_2 (ppm)	Sample No.	O_2 (ppm)
C-23A	- 296)*	C-36A	- 111
	306)		
	303 Average		

Test Laboratory No. 2 Results

Sample No.	O_2 (ppm)	Sample No.	O_2 (ppm)
C-23A	- 303	C-36A	- 129
"	- 219	"	- 193
"	- 230	"	- 137
"	- 263	"	- 117
"	- 247	"	- 133
"	- 232	"	- 83
"	- 233	"	- 139
	247 Average		133 Average
	84 Spread		110 Spread

*Duplicate Analysis

The accuracy of chemical analysis was further appraised by two other methods. First, 2-1/2" lengths of the 1" wide as-received strip were cut to 1/2" x 1" samples. The samples from one of the 2-1/2" lengths were submitted for oxygen determinations, those from the other 2-1/2" length for nitrogen determinations. Each of the 1/2" x 1" samples were again cut in half to 1/2" x 1/2" samples, one half for analysis in the as-received condition, the other after removal of a 2 mil surface layer. The results of five determinations for each condition displayed a scatter similar to that of the exposed samples.

Inasmuch as the average analyses for all samples in the as-exposed and 2 mil surface removed conditions were complete, and inasmuch as further analytical tests were found to be inexpedient, the average analyses were used to compare the effects of the various exposure conditions.

The bar graph shown as Figure 3 exhibits the oxygen results for the various temperatures and times at three levels of argon purity. The left portion of each bar represents the oxygen content of the sample in its as-exposed condition. The right hand portion after a 2 mil surface removal from each face. Bars which do not distinguish between left hand and right hand portions indicate the same results were obtained on the sample after a surface removal. The broken lines shown on some of the bars represent results of check analyses. Note that in some instances the analyses results were higher than initial results while in other instances they were lower. The bar at the extreme right of each series represents the results obtained on an unexposed strip sample in the as-received condition and after a 2 mil surface layer was removed.

The general information developed from this graph was:

1. Comparable analytical results for duplicate conditions (time-temperature-argon purity level) indicate analytical accuracy to be within 1 order of magnitude.

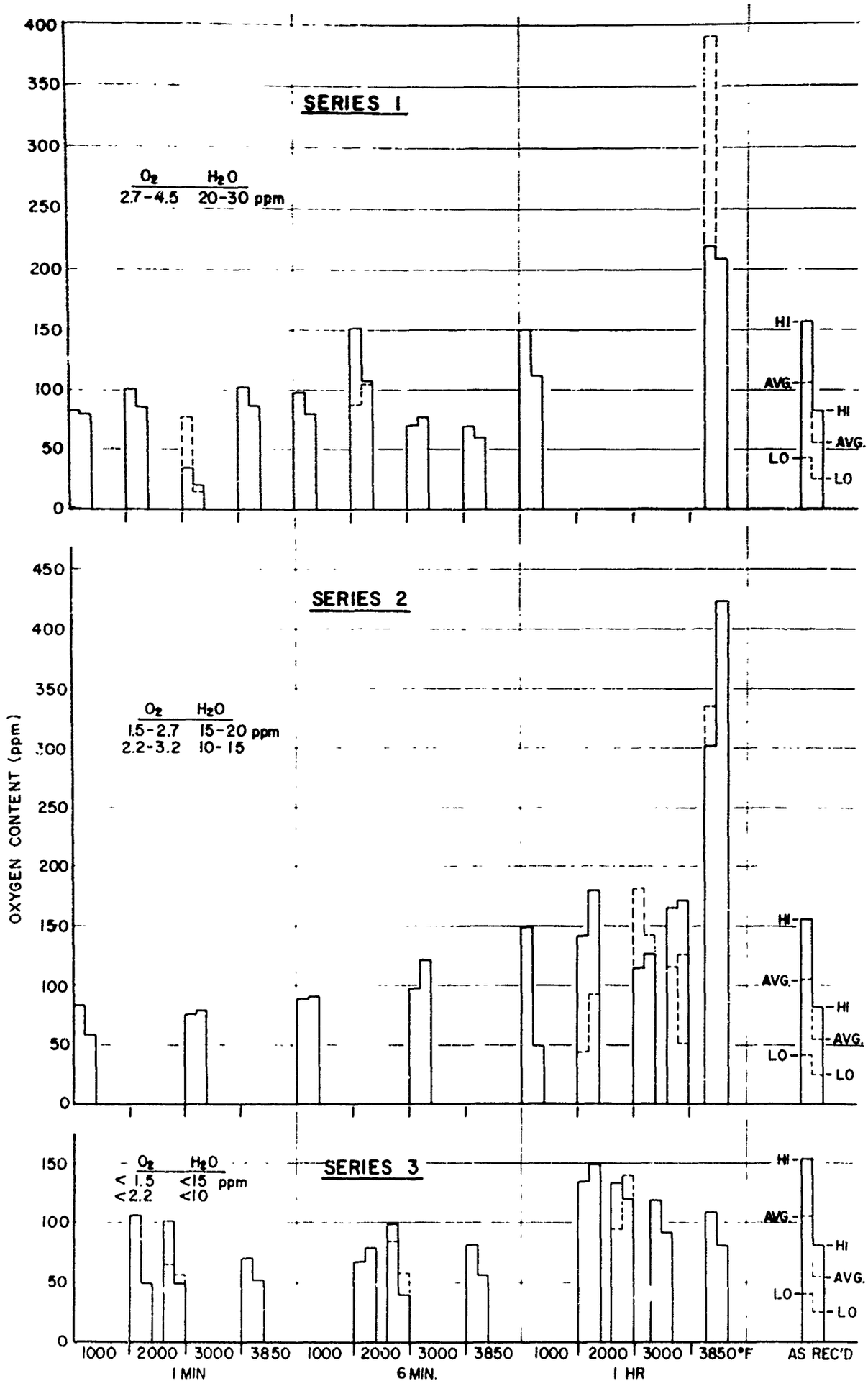


FIGURE 3

ANALYTICAL RESULTS (O_2) FOR Cb SAMPLES EXPOSED IN INFAB FOR INDICATED TIMES, TEMPERATURES AND ARGON PURITY LEVELS

2. The check analysis results indicate the analytical accuracy to be no better than 1 order of magnitude.

3. Differences between the results of as-exposed and surface removed conditions become smaller with improved argon purity levels.

4. Where the difference between the results of the as-exposed condition and those after a surface removal are within the difference range shown for the unexposed sample, it can be inferred that the actual differences are insignificant.

5. Oxygen pickup by Cb becomes less temperature and time dependent as the argon purity improves.

6. Exposures in the argon atmosphere of highest purity (about 2 ppm O_2 >10 ppm H_2O) level yielded all material as clean as it was in the as-received condition.

7. A significant effect was noted only for the "(1 hour at 3850°F)" study samples when the argon purity during the InFab exposure was at the level shown for the first and second series.

A similar graph shown as Figure 4 was plotted for the results of nitrogen determinations. The results compared with those for as-received material indicate that for all exposure conditions nitrogen pickup was negligible.

Of the 29 samples bend tested at -320°F to a sharp (O-T) bend radius and 105° bend angle, 7 had fractured. Of these 7, 6 were tested after surface removals of 1 to 2 mils before successful bends were accomplished. A comparison between the required surface removals and the respective analytical results for each of these samples showed no correlation. Two of the samples which required only 1 mil removal had significant differences in analytical results, and both showed lower values than those shown for some of the samples which did not fracture during the initial test run.

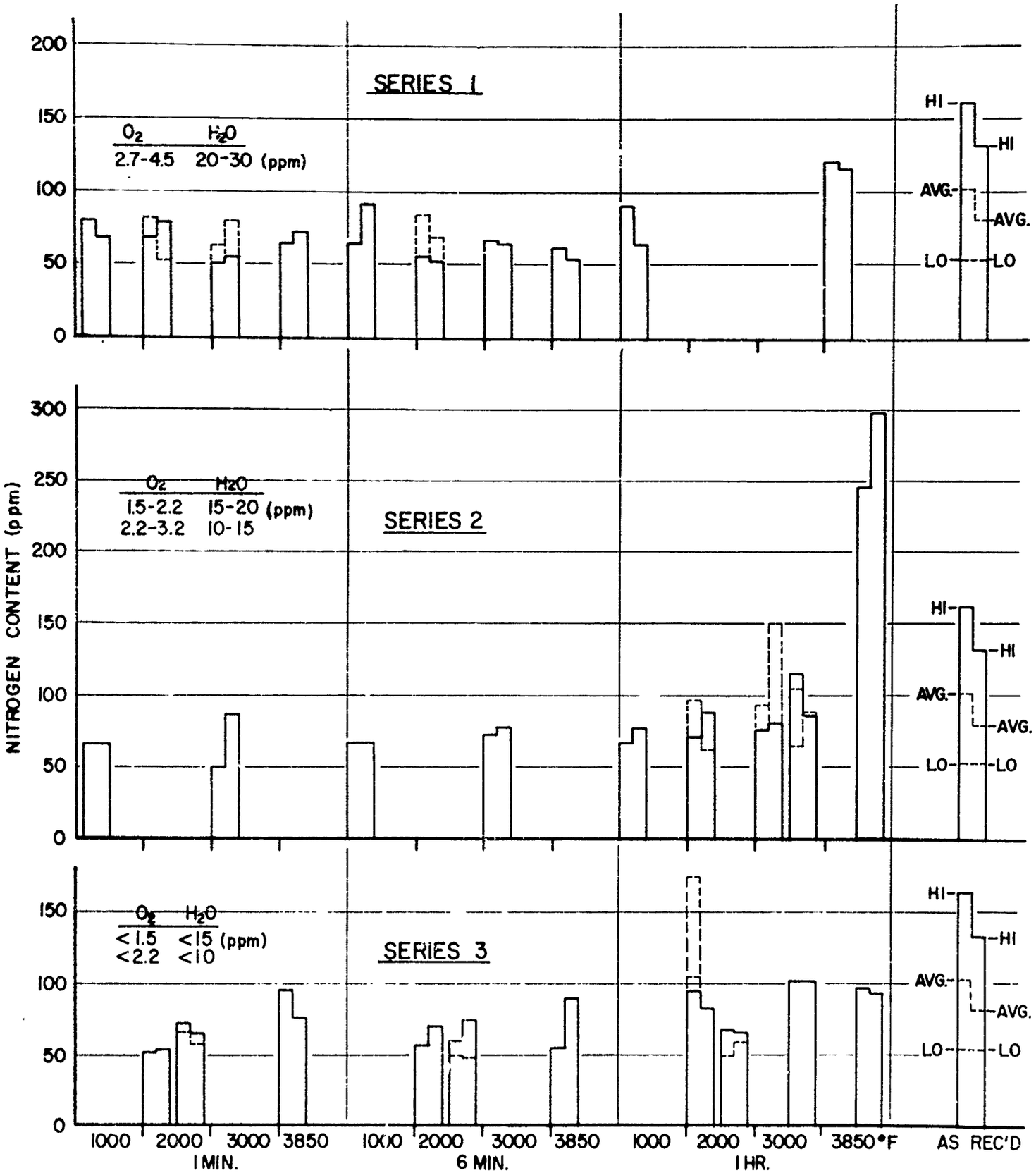


FIGURE 4

ANALYTICAL RESULTS (N_2) FOR Cb SAMPLES EXPOSED IN INFAB FOR INDICATED TIMES, TEMPERATURES AND ARGON PURITY LEVELS

The sample which required a 2 mil surface removal showed analytical values comparable to those of the sample requiring a 1 mil surface removal and showing the lowest analytical values of the 6 samples re-tested.

A comparison of bend results on these 6 samples with their exposure atmospheres also showed no correlation. Both of the samples exposed for 1 hour at 1000°F in argon of different purity levels required 1-1/2 mil surface removals and both of the samples exposed for 1 minute at 3850°F in argon of different purity levels required 1 mil surface removals. The facts that (1) no correlation existed between exposure conditions and analytical results for the six failures and that (2) all of the samples exposed at 2000°F exhibited successful bends regardless of exposures conditions, would suggest that factors other than contamination may be related to the bend test failures.

B. Tantalum Exposures

In an earlier report it was suggested that contamination of the tantalum study samples could not be serious inasmuch as the surface remained bright and clean. This assumption was based on the results reported by Kofstad and Krudtaa.[1] Their investigation showed that at oxygen pressures of 1 micron and temperatures above 1100°F Ta_2O_5 formed too rapidly a porous oxide scale which precluded measurements of the initiation of oxygen. The lack of any such oxide film on the InFab study samples indicates that the contaminating tendency of the argon in the first series of exposures could be no worse than a vacuum of 1 micron of oxygen.

The data for microhardness traverses performed only on the first and second series of Ta exposure samples were presented in the previous report. The hardness values could not be used to discriminate differences which could be attributed to contamination since other conditions appeared to have greater influence on hardness. This becomes evident when the analytical

results of the strip showing the highest hardness (309 KHN) at the surface and the greatest spread in values (118 KHN) were compared with the hardness and spread in values of a strip showing the highest pickup of oxygen. The analytical results reported for the strip showing high hardness and greater spread in values were essentially the same as reported for as-received material. The strip for which the highest oxygen pickup was reported showed a lower hardness at the surface (141 KHN) and a hardness spread of 16 and 30 KHN between surface to center readings for each of the strip faces. It was also noted that in general the hardness and hardness spreads for the exposed strip progressively diminished from those shown for the as-received material upon increasing time and temperature of exposure.

The analytical determinations for oxygen performed on Ta appeared to be of better accuracy than those for Cb. Although oxygen contents were reported higher after surface removals for 6 of 28 samples the differences were no greater than 16 ppm. Only a few check analyses were made and, since the divergences from initial analyses were no greater than the variations reported for the as-received material, further rechecks were not made. The variations on the as-received strip with no surface removal ranged from 9 ppm to 21 ppm oxygen and after a 2 mil surface removal 6 to 17 ppm oxygen.

The bar graph in Figure 5 indicated that:

1. The contaminating tendency by oxygen in the InFab argon atmosphere on Ta is less than that on Cb.

2. There is no evidence of contamination by oxygen occurring at 1000°F for a period up to 1 hour when the argon is at a purity level of <3.5 ppm O_2 and <20 ppm H_2O. At this purity level the contaminating tendency at temperatures up to 3000°F is slight for periods up to 1 hour.

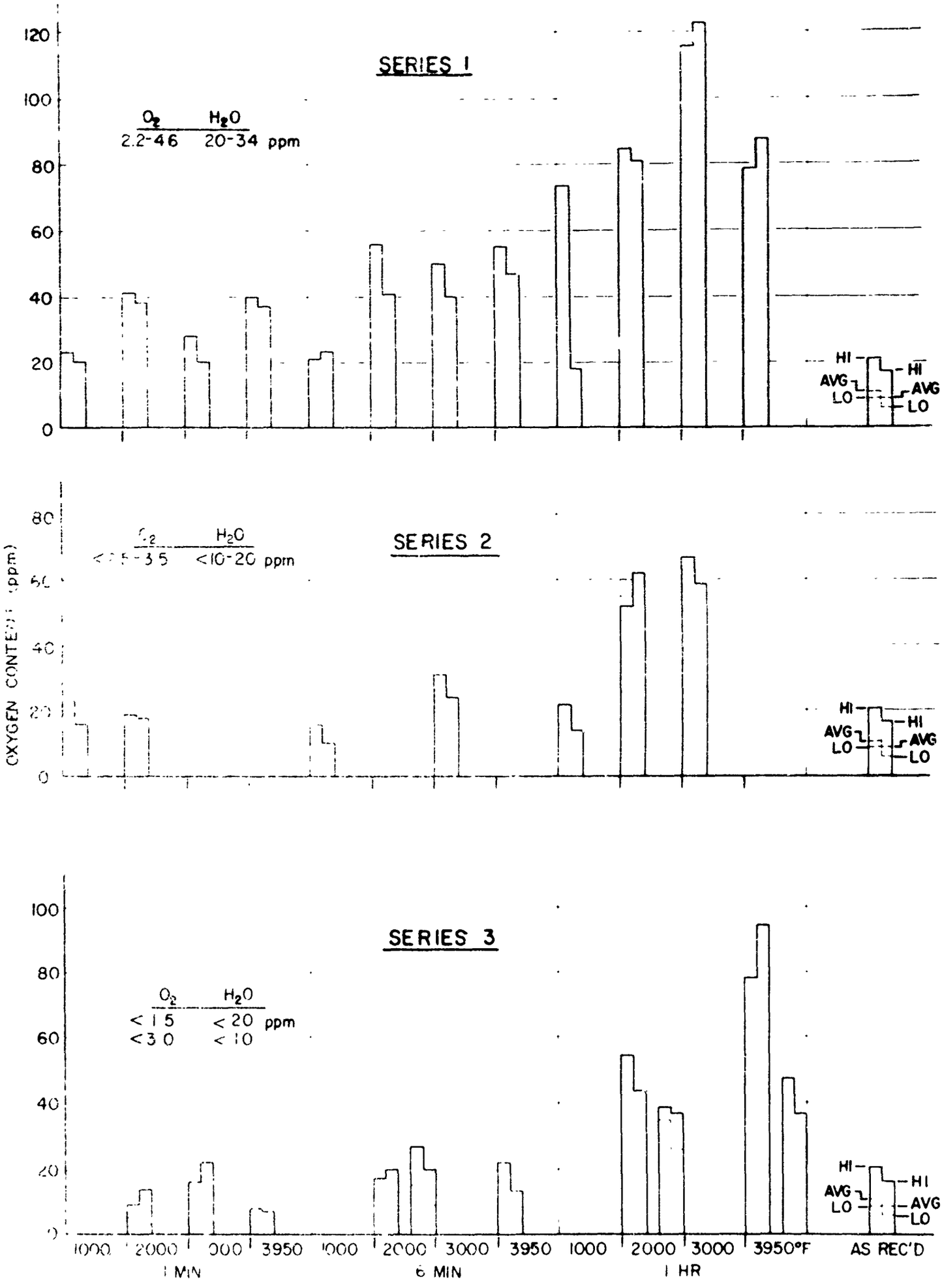


FIGURE 5

ANALYTICAL RESULTS (O_2) FOR Ta SAMPLES EXPOSED IN INFAB FOR INDICATED TIMES, TEMPERATURES AND ARGON PURITY LEVELS

3. At a higher purity level of <1.5 ppm O_2 and <20 ppm H_2O or <3 ppm O_2 and <10 ppm H_2O the contaminating tendency of InFab argon is slight at temperatures up to 3900°F and for periods up to 1 hour.

4. Regardless of the ratio of increase in oxygen over that reported for the as-received material, contamination - as defined earlier - is not serious (as defined by most Ta product specifications) at temperatures up to 3900 to 3950°F and for periods up to 1 hour when the InFab argon contains no more than 4.6 ppm O_2 and no more than 34 ppm H_2O.

From the analytical results illustrated by the bar graphs shown as Figure 6 it is quite evident that the contaminating tendency of nitrogen (5-7 ppm normal operating content) in the InFab argon is slight or non-existant on Ta exposed at temperatures to 3900°F and for periods up to 1 hour. The relatively high values shown for bars A and B are assumed to reflect either day to day analytical inaccuracy and/or variations in strip to strip of the as-recevied material. If one argues that bars A and B in Figure 6 indicate nitrogen contamination then the bars C, D and E would indicate purification. It is of interest to note the results for nitrogen determinations on a sample exposed for 1 hour in an InFab atmosphere containing approximately 3550 ppm of nitrogen. The sample identified on the bar graph as T-18 showed essentially no pickup of nitrogen by double check analysis and had excellent bend ductility (no flow cracks at -320°F and O-T bend radius test.)

The results of O-T-105° angle bend tests at -320°F were presented in the previous report. None of the samples failed. The only distinction noted between the various conditions was the presence of flow cracks which were described as surface distortion or grain boundary sliding. The presence of these flow cracks was also noted in the unexposed material.

NITROGEN CONTENT (ppm)

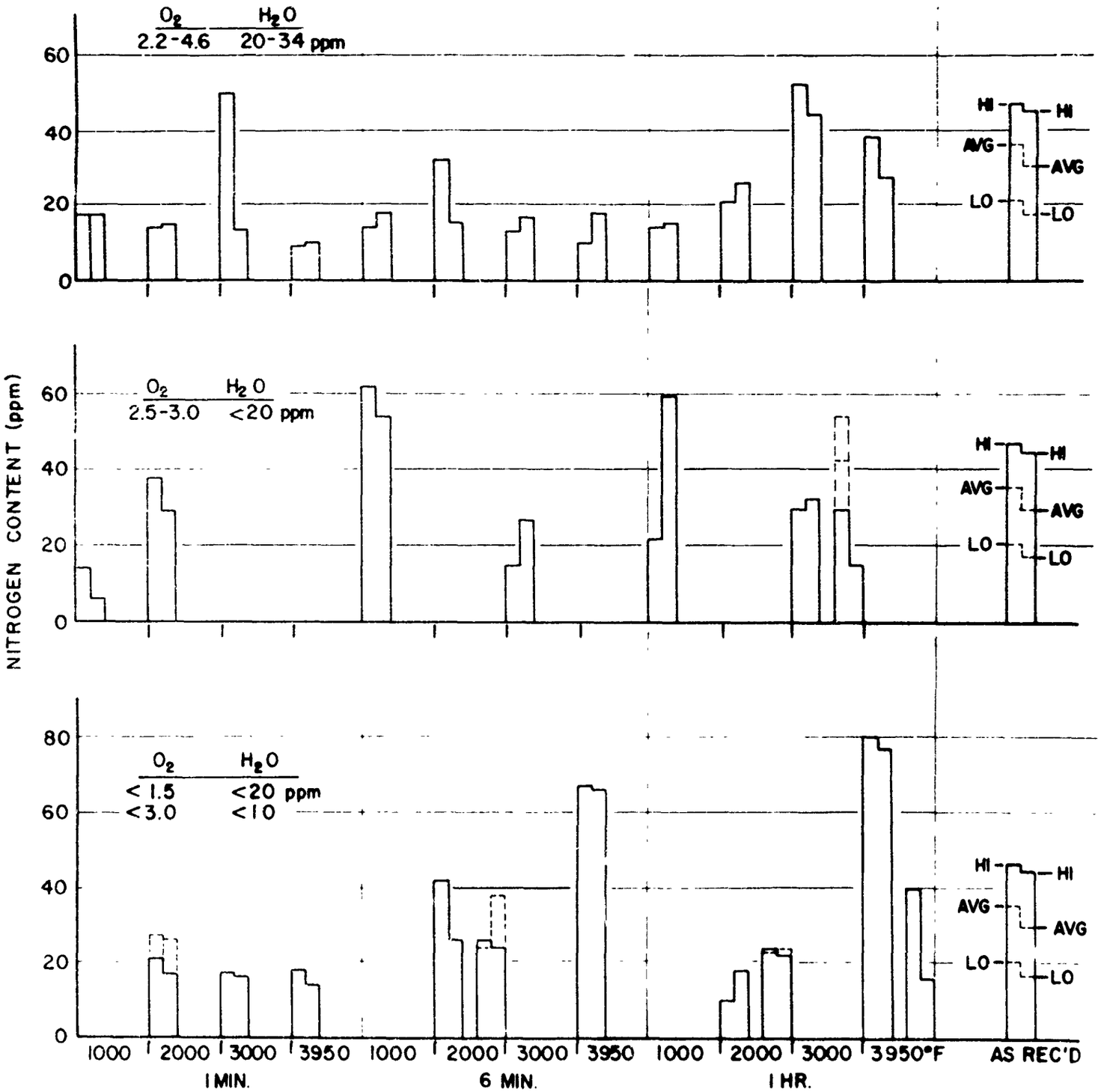


FIGURE 6

ANALYTICAL RESULTS (N_2) FOR Ta SAMPLES EXPOSED IN INFAB FOR INDICATED TIMES, TEMPERATURES AND ARGON PURITY LEVELS

The specimens which showed flow cracks were pickled to remove 1/2 mil from each surface in an effort to determine whether surface contamination was responsible for this condition. The results of this investigation showed no relationship existed between flow cracks and contamination. Both improvements and no improvements were noted for samples having comparable low values of oxygen and nitrogen contents, and likewise, improvements and no improvements were noted for samples having comparable higher values of oxygen and nitrogen contents.

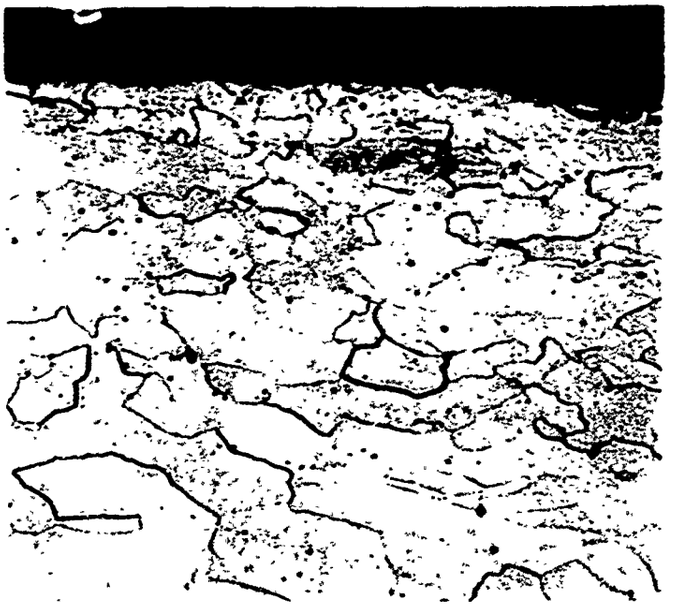
C. B-66 Exposure Samples

Microhardness traverses reported for the first and second series of exposures in the previous report were not continued on the third series of samples. This test procedure was relinquished when variations in hardness readings were in the range which could only be related to microstructural or stress-strain differences.

In the previous report photomicrographs of exposure samples were presented without much discussion except the information delivered by the testing laboratory. The laboratory interpretation of the dark etching zone appearing in the 2000°F exposures as being a contamination layer did not appear to be valid. It was highly doubtful that contamination or film formation would proceed in such fashion as to by-pass or isolate some grains (not darkened) within the supposed contamination (dark zone) layer. From this observation and the chemical analysis it was deduced that the dark zone was an etching phenomena possibly related to polishing technique or material processing history. The samples were then repolished and etched by a procedure recommended by the material producer. As shown by photomicrographs in Figure 7 the dark etching zone did not re-appear in the samples exposed at 2000°F.

Mention also had been made in the previous report that the internal oxidation observed in samples exposed at 3000°F was spotty and might be attributed to presence of contamination film or spotty areas on the as-received strip. Metallographic samples

R10780 B-3 500X



R10779 B-25 500X

R10778 B-30 500X

FIGURE 7

Photomicrographs of B-66 Samples Exposed in InFab for 1 Hour Periods at 2000°F

taken of unexposed material confirmed that spotty contamination existed in the as-received material. Photomicrographs shown as Figure 8 illustrate the presence of this condition.

Check analyses performed on a few samples reflected a similar situation with regard to accuracy as was experienced for Cb. Since it had become obvious that further checks would not assure accuracy this situation was not pursued. As in previous graphs the check analyses are shown as broken-line bars.

From the results of oxygen determinations plotted as bar graphs in Figure 9 for the three levels of argon purity, it becomes evident that:

1. For comparable levels of atmosphere purity, the contaminating tendency on B-66 for periods up to 1 hour and temperatures up to 3000°F is similar to that on unalloyed Cb.

2. For temperatures above 3000°F the contaminating tendency on B-66 for comparable exposure conditions is less than that on Cb.

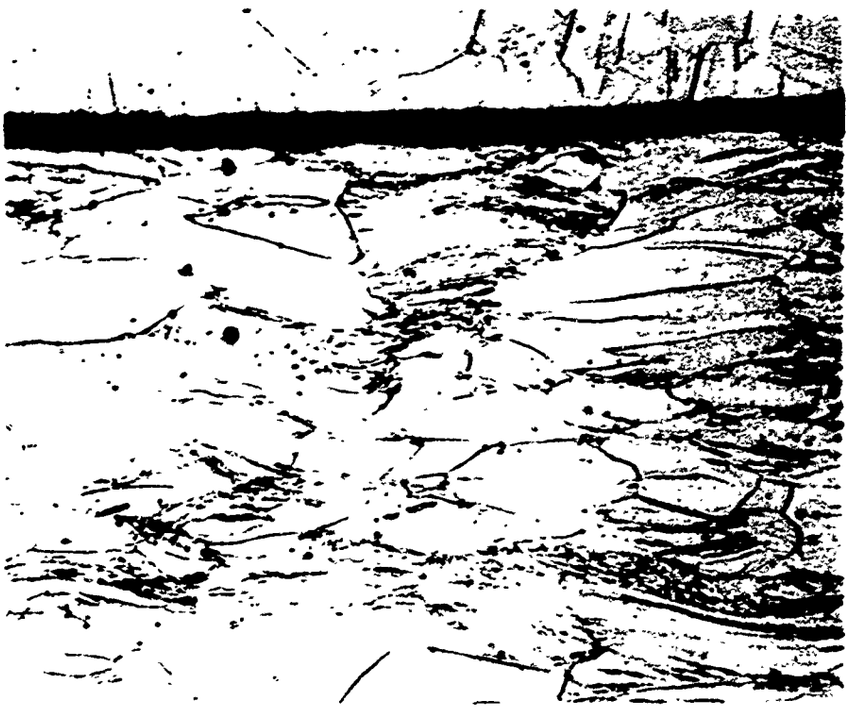
3. The contaminating tendency is negligible for periods up to 1 hour and temperatures to 1000°F when the argon purity level is no worse than 4.7 ppm O_2 and 34 ppm H_2O.

4. At a higher purity level of argon its contaminating tendency is not serious (as defined by present product specifications) at temperatures to 3600°F and for periods up to 1 hour.

5. At a purity level of <2 ppm O_2 and <10 ppm H_2O in argon, the contaminating tendency is negligible or non-existent for temperatures up to 3600°F and for periods up to 1 hour.

The analytical results for nitrogen shown plotted in Figure 10 indicate:

1. There is essentially no difference in nitrogen pickup between the three levels of argon purity.



R9992 500X

Sample Taken From Area Not
Appearing Contaminated

R10776 500X

Sample Taken From Area
Appearing Contaminated

FIGURE 8

Photomicrographs Showing the Existance of
Contaminated Areas on As-Received B-66 Strips

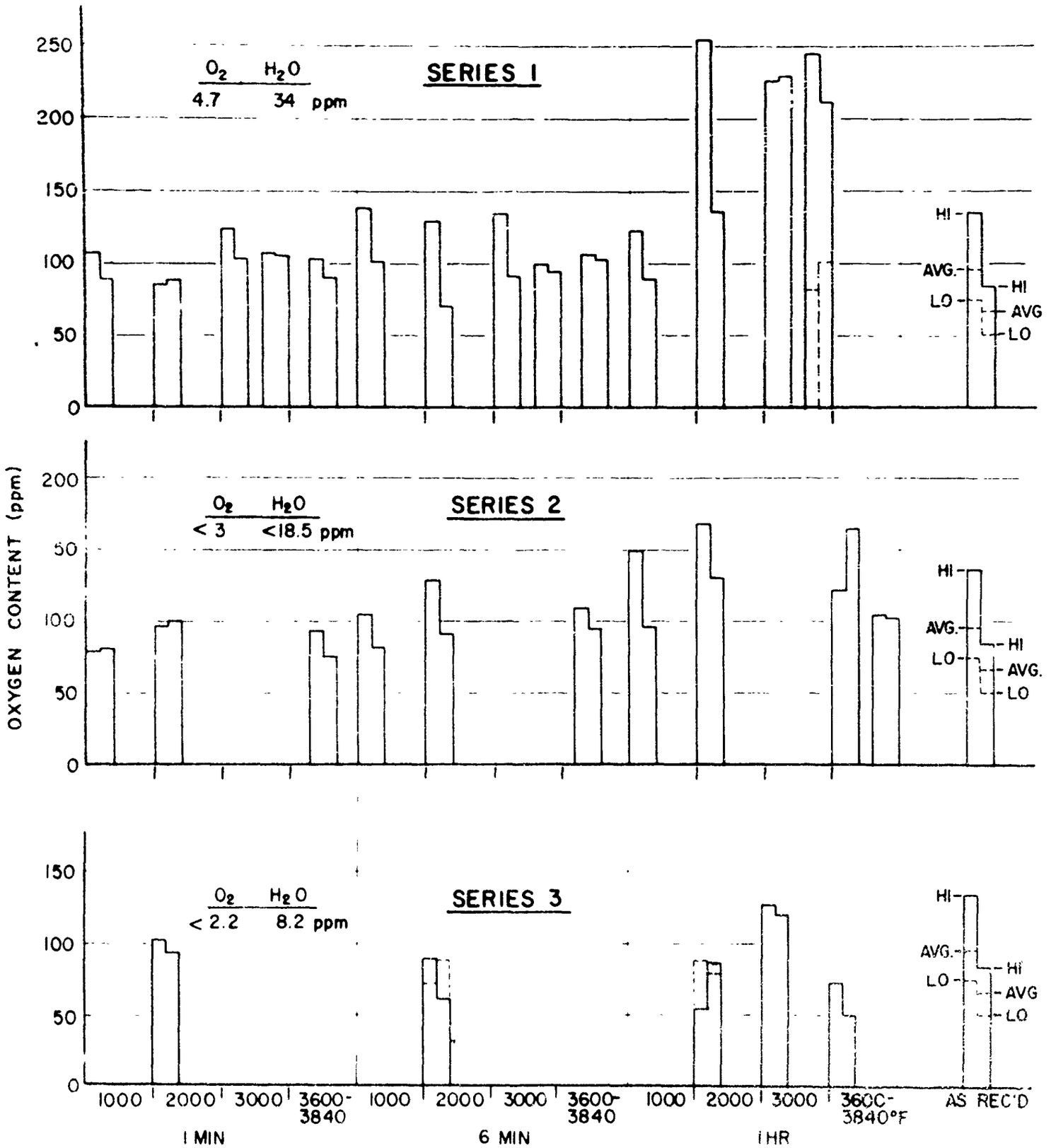


FIGURE 9

ANALYTICAL RESULTS (O_2) FOR B66 SAMPLES EXPOSED IN INFAB FOR INDICATED TIMES, TEMPERATURES AND ARGON PURITY LEVELS

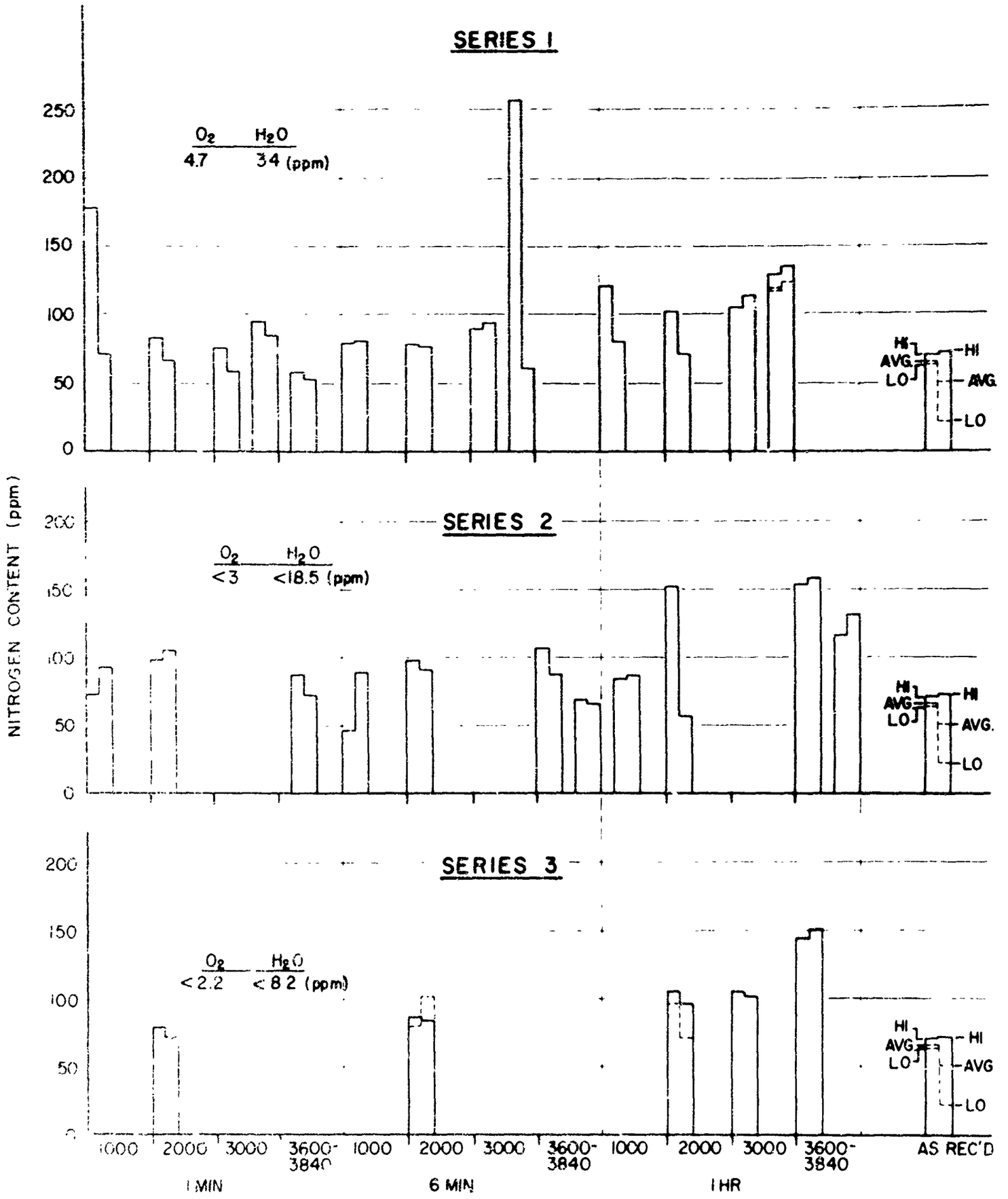


FIGURE 10

ANALYTICAL RESULTS (N_2) FOR B66 SAMPLES EXPOSED IN INFAB FOR INDICATED TIMES, TEMPERATURES AND ARGON PURITY LEVELS

2. Contamination by nitrogen in the InFab argon does not appear to be serious for periods up to 1 hour and temperatures up to 3840°F.

From the bend test results shown in Table II the following observations were made:

1. B-66 is structure sensitive to bend ductility. Anneals in the range of 2000°F are required to relieve the adverse stress-strain effects induced by working. This was evident on as-received material and on the 1000°F exposure samples which showed transition temperatures above 600°F but after a 2000°F anneal showed transition temperatures ranging from -100 to -320°F. It is of importance to note that the transition temperatures exhibited by these samples before the anneal could not be lowered with surface removals. Bend ductility of B-66 is also adversely affected by grain coarsening which occurs rapidly at 3000°F and above.

2. Inasmuch as no correlation could be found between bend test results and analytical data or argon purity for samples exposed at temperatures of 1000°F, 3000°F and 4000°F, improvements in bend test results after surface removals are probably attributed to relaxation of adverse structural factors with improved surface condition.

3. The great improvements in bend ductility after 2 mil surface removals for some of the samples exposed at 2000°F would at first suggest contamination to be 2 mils deep. However, the results of the investigation which revealed the presence of contamination on as-received material and the observations discussed in the above paragraph, suggest that the adverse effect of the surface layer was not due to interstitial pickup during InFab exposure. The excellent bend results obtained for the series 3 exposures at 2000°F along with low analytical results for these samples demonstrates that the contamination existing on the as-received material as illustrated by its representative bar in Figure 9 could have been removed or dispersed by further diffusion during exposure.

TABLE II

BEND TEST DATA (2T-105° BEND ANGLE) FOR B66 SAMPLES EXPOSED IN INFAB TO INDICATED CONDITIONS

Condition	Spec.	Series	As Exposed		2 Mils Removed	
			X	O	X	O
1 min. - 1000°F	B-8	I	600°F	-	600°F	-
1 " "	B-18	II	600	-	600	-
6 min. - 1000°F	B-7	I	600	-	600	-
6 " "	B-17	II	600	-	600	-
1 hr. - 1000°F	B-9	I	600	-	600	-
1 " "	B-19	II	600	-	600	-
1 min. - 2000°F	B-2	I	-20	0°F	-320	-240°F
1 " "	B-24	II	-20	0	-200	-130
1 " "	B-31	III	-240	-200	-320	-240
6 min. - 2000°F	B-1	I	-70	-55	-320	-240
6 " "	B-23	II	-80	-65	-320	-240
6 " "	B-29	III	-240	-200	-	-320
1 hr. - 2000°F	B-3	I	-150	-120	-320	-240
1 " "	B-25	II	-150	-125	-320	-240
1 " "	B-30	III	-320	-240	-320	-240
1 min. - 3000°F	B-5	I	60	80	-240	-190
1 " "	B-16	I	300	325	0	50
6 min. - 3000°F	B-6	I	200	240	0	25
6 " "	B-15	I	175	200	-40	0
1 hr. - 3000°F	B-4	I	300	340	250	300
1 " "	B-14	I	400	425	350	400
1 " "	B-32	III	175	200	150	200
1 min. - 3840°F	B-12	I	105	130	0	35
1 " 3600°F	B-28	II	600	-	0	25
6 min. - 3600°F	B-26	II	275	300	0	25
6 " "	B-11	II	160	175	0	35
1 hr. - 3840°F	B-10	II	-150	-140	-130	-110
1 " 3600°F	B-27	II	225	250	110	175
1 " 3820°F	B-37	III	600	-	600	-
As received	B-0		600	-	600	-

X Denotes Failure

O Denotes Successful Bend

D. TZM Exposures

Of the four materials used in this program, the TZM alloy is most structure sensitive; therefore, the hardness traverses performed on the first series were not continued on the second and third series. Samples exposed above the recrystallization temperature (3000°F to 4000°F) did not show differences between surface and center readings which would indicate contamination.

Metallographic examination of the exposure samples did not reveal presence of contamination. It should be understood that detection of contamination in the worked structures of TZM is difficult and would require heat-treatment to effect a recrystallization difference between the contaminated and uncontaminated zones. The typical microstructures for the four exposure temperatures were exhibited in the previous report.

Chemical analyses data for oxygen and nitrogen contents were plotted as bar graphs in Figures 11 and 12 for three series of exposures. The solid line bars represent the initial analyses and the broken line bars represent the check analyses. The differences between initial analyses and check analyses along with variations in results for as-received strip demonstrate the accuracy which could be expected. Within this limit of accuracy the bar graphs depicting oxygen determinations indicate that:

1. The contaminating tendency on TZM is not serious when the argon purity is at a level of <4.8 ppm O_2 and <32 ppm H_2O.

2. In an argon purity level of <3 ppm O_2 and <25 ppm H_2O, the contaminating tendency is negligible for periods up to 1 hour and temperatures up to 4000°F.

3. At a temperature of 4000°F purification may occur in argon containing oxygen of no more than 3 ppm and H_2O no more than 20 ppm.

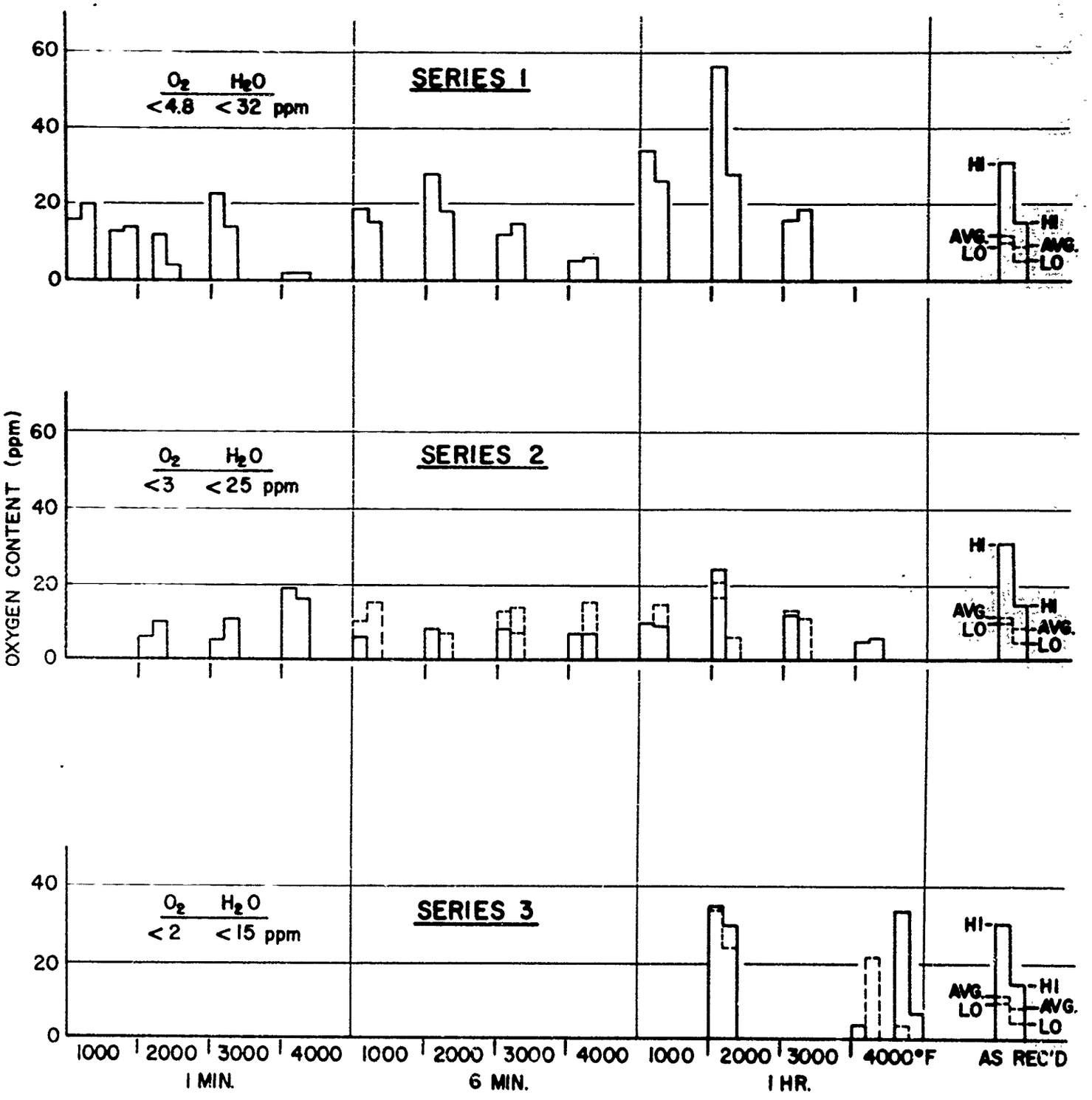


FIGURE 11

ANALYTICAL RESULTS (O_2) FOR TZM SAMPLES EXPOSED IN INFAB FOR INDICATED TIMES, TEMPERATURES AND ARGON PURITY LEVELS

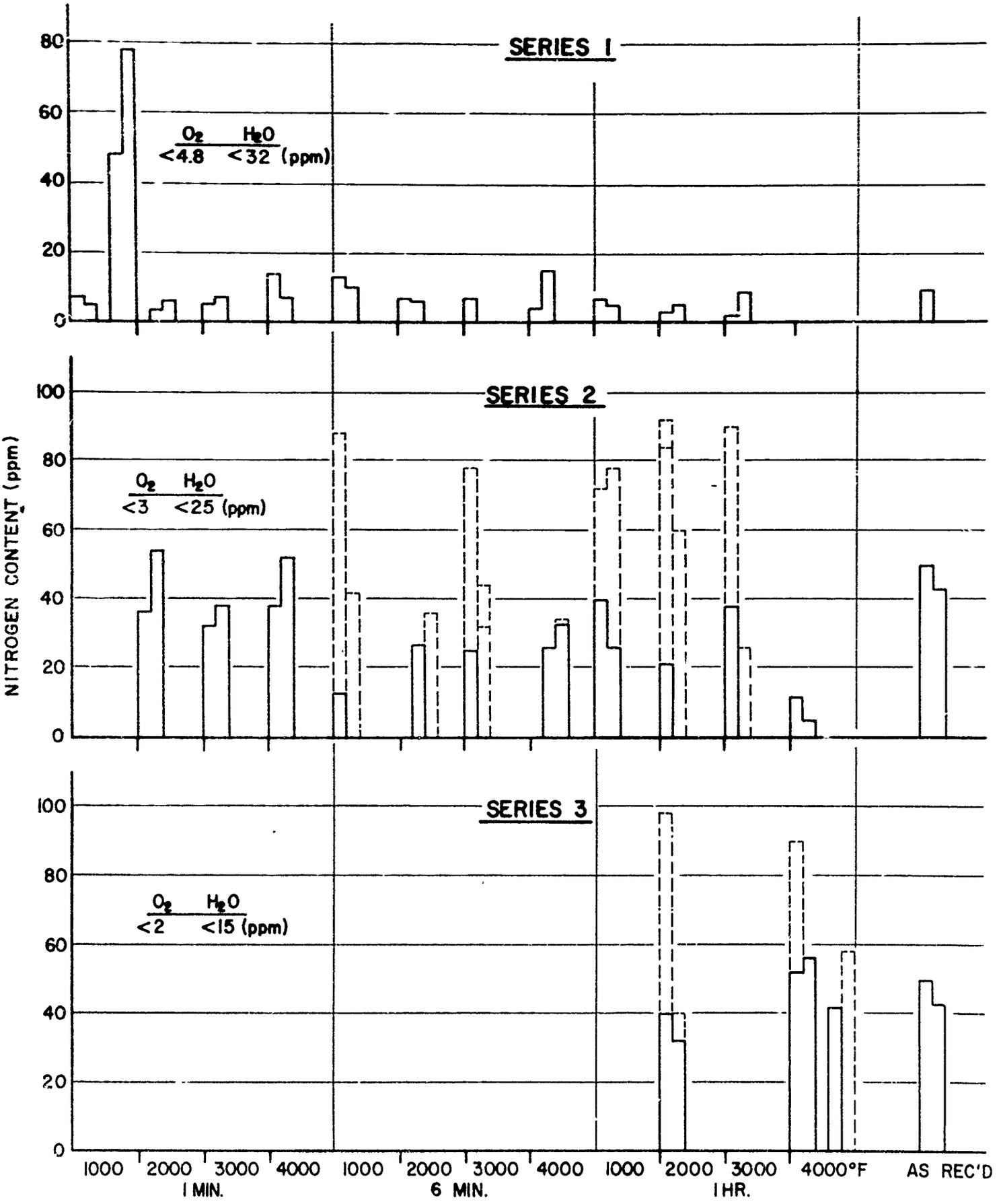


FIGURE 12

ANALYTICAL RESULTS (N_2) FOR TZM SAMPLES EXPOSED IN INFAB FOR INDICATED TIMES, TEMPERATURES AND ARGON PURITY LEVELS

The analytical results for nitrogen determinations presented a perplexing situation. The results of three lots submitted on different days were succeedingly higher on later dates of analysis. The first lot of samples represented the first series of exposures. The highest nitrogen results reported for this series of exposures was 15 ppm. This compared favorably with results of 9 ppm reported for as-received material submitted with this lot.

The second lot of submitted samples represented the second and third series of exposures. The results reported for this lot were higher than those reported for the first lot by several orders of magnitude. The same order of magnitude increase was reported for an as-received sample submitted with this lot.

Inasmuch as the second lot of samples analyzed represented exposures to higher purity atmospheres, a check analysis was warranted. Most of the samples exposed in the second and third series were then submitted for analysis as a third lot. An as-received sample was not submitted with this lot.

The check analysis results (third lot) were reported even higher than those reported earlier (second lot) by several orders of magnitude.

The results of the above mentioned analyses are shown by the bar graph in Figure 12. With the exception of one bar (1 min. at 1000°F) showing high values, the bars representing results obtained for the first lot of samples are shown as series I. The bars representing samples exposed to higher purity argon and submitted for analysis as a second lot are shown as series II and as series III. The check analysis results shown for the second and third series represent the lot submitted at a later date.

By comparing the results of the exposure samples with the results of respective as-received test samples and taking into account the limits of accuracy as demonstrated by check results, it becomes apparent that nitrogen pickup for all conditions is undefinable.

The results of bend tests (2T bend radius -105° angle) shown in Table III indicated that:

1. TZM is highly structure sensitive to bend ductility hence this method for measuring contamination is unreliable.

2. Since no correlation could be found between bend test results and atmosphere purity level or analytical results, and since only slight improvements were noted in some samples, this slight improvement may be attributable to improvement of texture or surface roughness.

IV. Evaluation of Time-Temperature-Work Samples

The analytical results for interstitial contents of the rolled strip samples presented in the previous report are shown plotted as bar graphs in Figure 13. To the left of each series of bars representing a particular strip material are bars illustrating the high, low and average values reported for the as-received strip. The left portion of the bars for the rolled material represent analysis for the as-rolled condition. The right hand portions represent analysis after a 2 mil surface removal. The solid line bars represent analyses for strip rolled at 1400°F. The broken line bars represent analyses for strip rolled at 2000°F. The total exposure times and number of passes given each of the strips are posted below the respective bars.

The bar graph shown in Figure 13 illustrates that oxygen and nitrogen pickup during rolling was very slight or non-existent for both rolling temperatures and for all 4 materials, Cb, Ta, TZM and B-66. Iron pickup on the other hand was appreciably higher than interstitial pickup. It should be noted that the data obtained is pertinent only to rolling with bare rolls and with no lubricant. The analytical results are shown plotted in Figure 14 in the same manner as those shown in Figure 13. From the bar graph in Figure 14 it is evident that:

TABLE III

BEND TEST DATA (2T-105° BEND ANGLE) FOR TZM SAMPLES EXPOSED IN INFAB TO INDICATED CONDITIONS

Condition	Spec.	Series	As Exposed		2 Mils Removed	
			X	O	X	O
1 min. - 1000°F	M-10	I	-200°F	-170°F	-200°F	-180°F
1 " "	M-26	I	-120	-100	-200	-180
6 min. - 1000°F	M-9	I	-200	-170	-200	-180
6 " "	M-24	II	-320	-240	-320	-240
1 hr. - 1000°F	M-11	I	0	20	0	20
1 " "	M-25	II	75	120	-40	0
1 min. - 2000°F	M-7	I	-100	-85	-200	-130
1 " "	M-18	II	-200	-170	-240	-200
6 min. - 2000°F	M-6	I	-100	-85	-240	-200
6 " "	M-19	II	20	35	-40	0
1 hr. - 2000°F	M-5	I	-150	-120	-200	-130
1 " "	M-20	II	0	35	-110	-70
1 " "	M-27	III	-65	-40	-130	-110
1 min. - 3000°F	M-2	I	0	20	-70	-40
1 " "	M-15	II	45	55	0	25
6 min. - 3000°F	M-3	I	20	40	0	20
6 " "	M-16	II	55	75	25	50
1 hr. - 3000°F	M-4	I	20	50	20	50
1 " "	M-17	II	35	55	35	55
1 min. - 4000°F	M-13	I	350	375	350	375
1 " "	M-23	II	400	425	400	425
6 min. - 4000°F	M-14	I	325	350	325	350
6 " "	M-22	II	400	425	400	425
1 hr. - 4000°F	M-12	II	350	375	350	375
1 " "	M-21	III	300	320	250	300
1 " "	M-33	III	300	325	300	325
As received	M-0			-85		

X Denotes Failure

O Denotes Successful Bend

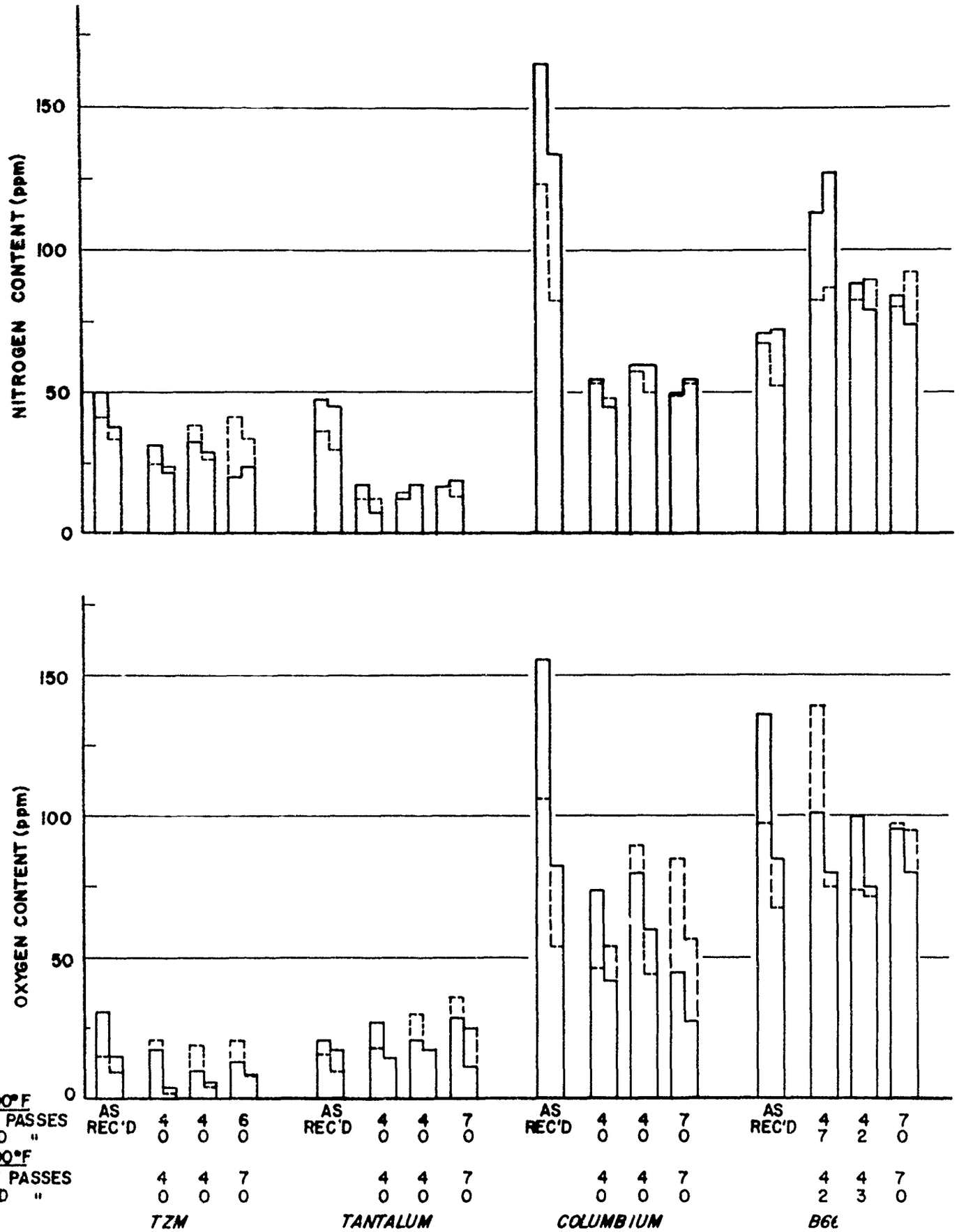


FIGURE 13

ANALYTICAL RESULTS (O_2 & N_2) FOR REFRACTORY METAL STRIPS ROLLED IN INFAB AT INDICATED TEMPERATURES AND PASS SCHEDULES

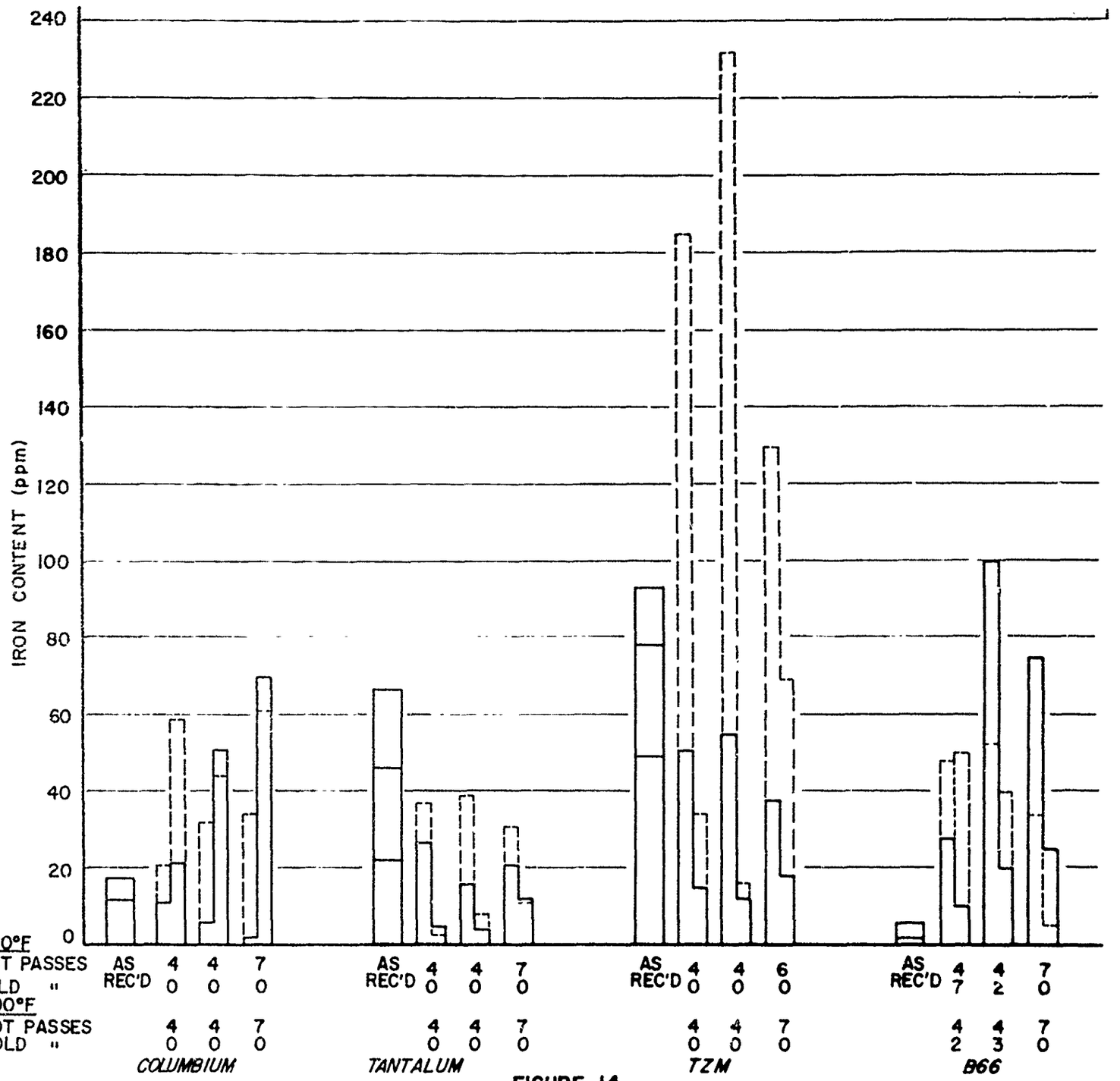


FIGURE 14

ANALYTICAL RESULTS (Fe) FOR REFRACTORY METAL STRIPS ROLLED IN INFAB AT INDICATED TEMPERATURES AND PASS SCHEDULES

1. At rolling temperatures of 1400°F the iron pickup results for Ta and TZM compare favorably with the results for the respective as-received strip. The higher results after surface removals for the Cb samples strongly reflect analytical inaccuracy.

The increase of iron content over the as-received content for the B-66 rolled at 1400°F could be attributable to the galling tendency of this material to rolls when high pressures are used. Several cold passes with high roll pressures had to be given to each of these strips to accomplish the desired reduction and the iron pickup may have occurred during this cold rolling. The extent of iron pickup during cold rolling shall be investigated for all four materials on the next portion of this phase of the program.

2. At a rolling temperature of 2000°F appreciable iron pickup was noted only for the TZM and B-66 strip. Note that at this temperature iron pickup for B-66 was less than it was for the 1400°F temperature. It is of interest to note that the iron pickup on B-66 given 7 heats at 2000°F with no cold passes showed less iron pickup than the samples rolled at this temperature with final cold passes.

Bend tests on the Cb and Ta samples in the as-rolled condition were performed at -320°F using a sharp 0-T bend radius and 105° bend angle. With the exception of one Cb sample, all others were successfully bent The columbium sample (C1-x rolled at 1400°F) which failed in the as-rolled condition did not fail after removal of a 2 mil surface layer.

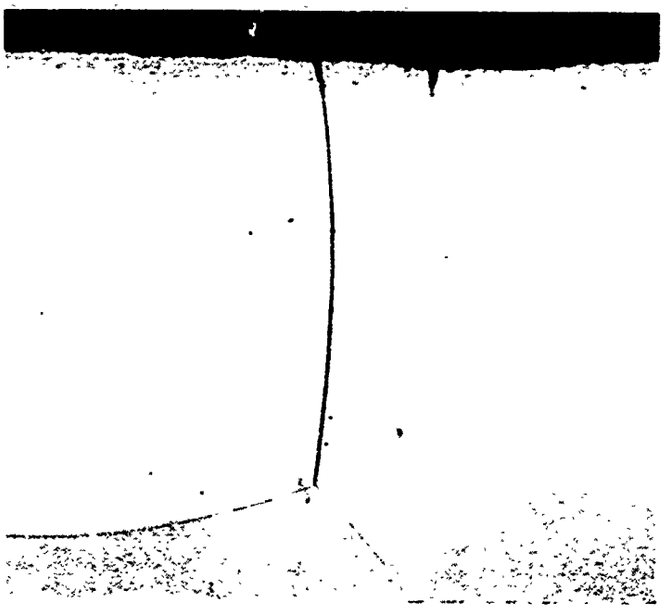
All of the B-66 and TZM samples failed a 2T bend test at 600°F in the as-rolled condition and after 2 mil surface removals. In an effort to obviate the evident structural effects so that depth of contamination could be investigated, the samples were vacuum annealed at 2200°F for 15 minutes. A B-66 test sample which previously had been exposed in InFab at 3840°F was included with this anneal.

Another lot of B-66 and TZM rolled samples were vacuum annealed for 15 minutes at 2600°F to effect a partial recrystallization for metallographic examination. A B-66 test sample which had been previously exposed in InFab at 3840°F was also included in this anneal.

Upon metallographic examination of the test samples it was discovered that contamination had occurred during both vacuum anneals. The extent of this contamination is illustrated in Figure 15 by photomicrographs of the B-66 test sample before and after the anneals.

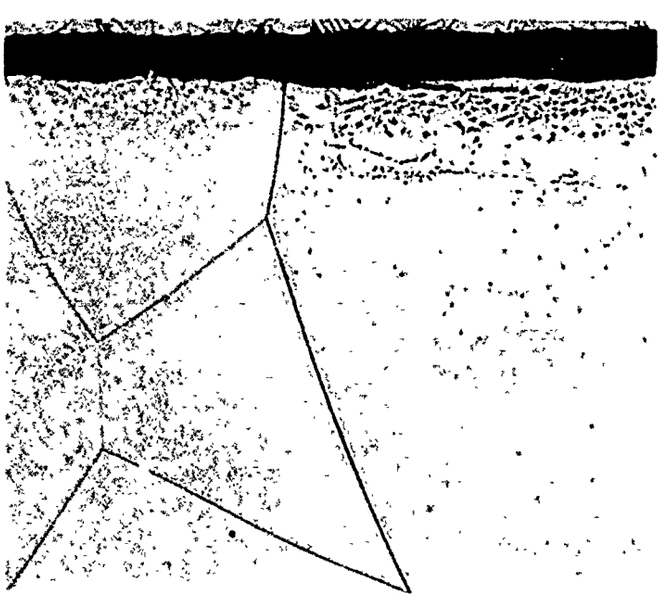
The occurrence of contamination on the rolled B-66 samples is shown by photomicrographs in Figure 16. That this contamination occurred during the vacuum anneal was corroborated by chemical analysis. To prevent obscurity which could result from fluctuations of analytical accuracy during different times, samples not annealed (R.T. bend test samples) were submitted for chemical analysis with the lot of annealed samples. The resulting analytical results shown in Table IV establish that contamination did occur on all vacuum annealed material.

The samples which were vacuum annealed at 2200°F for 15 minutes were bend tested without surface removals prior to discovery that they had become contaminated during the anneal. It was of much interest to note that despite this contamination the transition temperature was lowered for both TZM and B-66 by several hundred degrees as shown in Table V. This great improvement in bend ductility strongly supports the argument used on page 24 that conditions other than contamination may have as strong or stronger effect on the bend ductility of B-66. As a result of the contamination which occurred on the vacuum annealed rolled samples, further bend testing on these samples was abandoned.



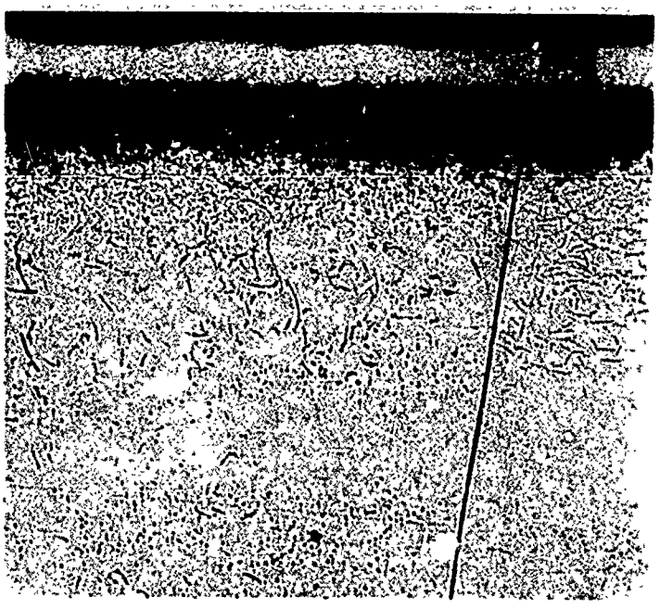
R15038 500X

Sample Exposed in InFab @ 3850°F



R11015 250X

Vacuum Annealed
15 Minutes @ 2200°F

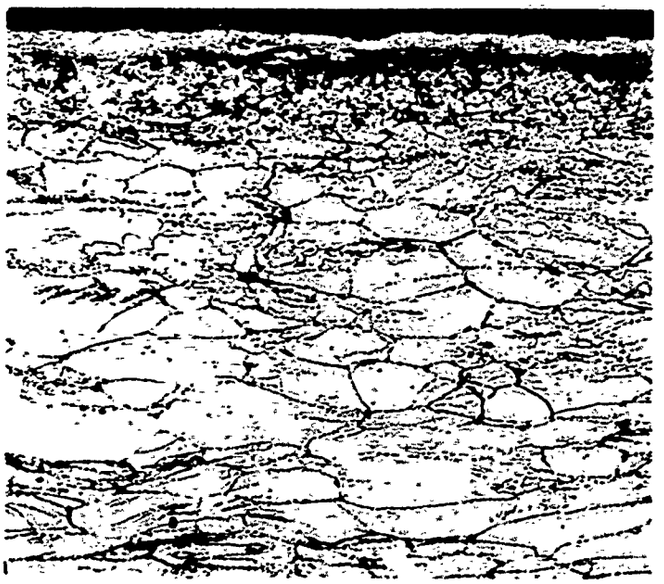


250X

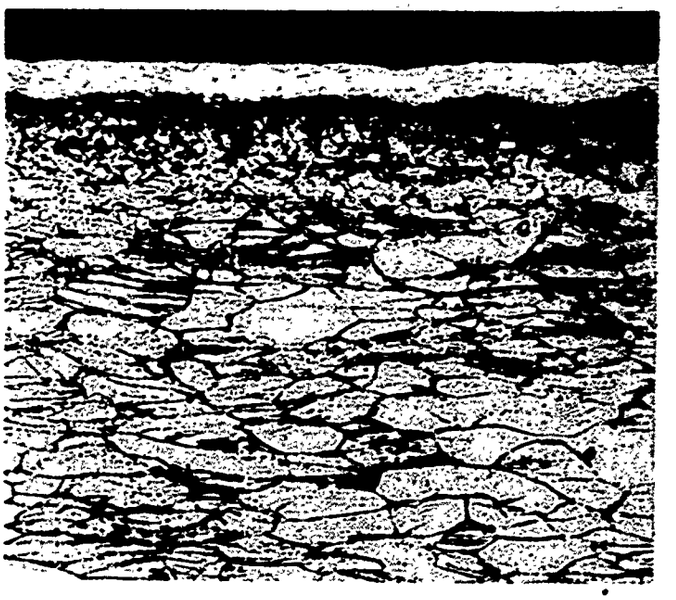
Vacuum Annealed
15 Minutes @ 2600°F

FIGURE 15

Photomicrographs of B-66 Samples Showing
Progress of Contamination During Vacuum Anneal

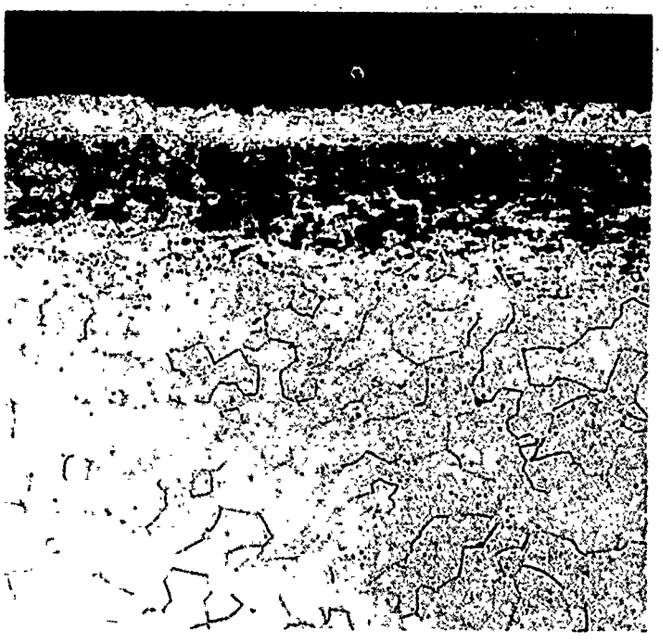


11010 B2Y 250X

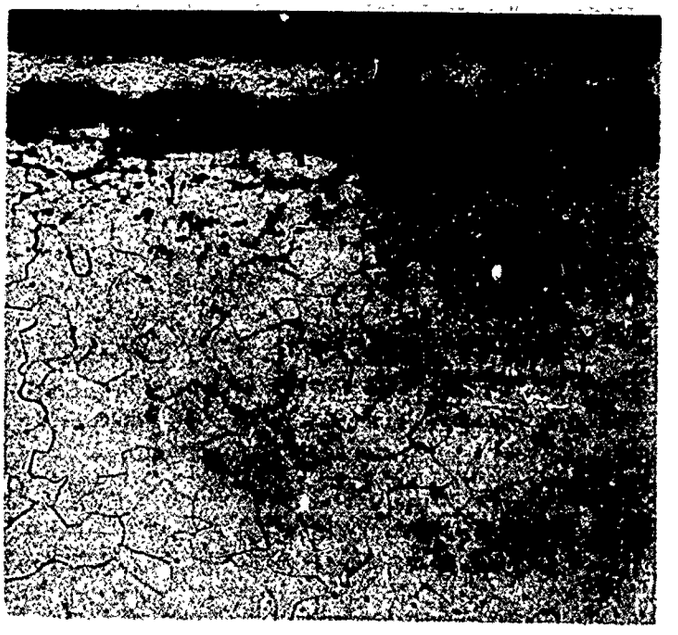


11011 B1Z 250X

Annealed 15 Minutes @ 2200°F



11012 B2X 250X



11014 B2Z 250X

Annealed 15 Minutes @ 2600°F

FIGURE 16

Photomicrographs Showing Contamination Layers on B-66 Rolled Samples After Indicated Vacuum Anneals

TABLE IV

ANALYTICAL RESULTS INDICATING CONTAMINATION
OCCURRED ON B66 AND TZM ROLLED SAMPLES
DURING ANNEALS IN VACUUM OF 0.1 MICRONS

B66 Samples Annealed 15 min. at 2200°F

Sample	O_2 (ppm) Before Anneal	O_2 (ppm) After Anneal
B1 X	158	237
B2 Y	151	236
B2 Z	176	237

TZM Samples Annealed 15 min. at 2600°F

Sample	O_2 (ppm) Before Anneal	O_2 (ppm) After Anneal
M2 X		158
M3 X	45	100
M3 Y		76
M2 Z		138,134
M3 Z	47	135

TABLE V

BEND TEST (2T-105° BEND ANGLE) RESULTS ON B66 AND TZM AS ROLLED SAMPLES BEFORE AND AFTER VACUUM ANNEAL AT 2200°F FOR 15 MIN.

B66 Samples

Sample No.	Rolling Temp. °F	Before Anneal		After Anneal	
		X	0	X	0
B1 X	1400	600°F	-	-100°F	-75°F
B1 Y	1400	600°F	-	-40°F	-25°F
B1 Z	1400	600°F	-	-	-100°F
B2 X	2000	600°F	-	-100°F	-75°F
B2 Y	2000	600°F	-	-100°F	-75°F
B2 Z	2000	600°F	-	-	-100°F

TZM Samples

Sample No.	Rolling Temp. °F	Before Anneal		After Anneal	
		X	0	X	0
M2 X	1400	600°F	-	175°F	200°F
M2 Y	1400	600°F	-	175°F	200°F
M2 Z	1400	600°F	-	300°F	-
M3 X	2000	600°F	-	75°F	125°F
M3 Y	2000	600°F	-	200°F	250°F
M3 Z	2000	600°F	-	75°F	125°F

X Denotes Failure

O Denotes Successful Bend

V. Inert Atmosphere Versus Vacuum Exposure

From the analyses of the data in Figure V it becomes evident that the contaminating tendency of the InFab atmosphere may be no worse than that of commercially available vacuum systems of much lower partial pressures of oxygen.

H. Inouye[2] in his investigation of the oxidation of Cb at low pressures of oxygen in vacuum found that:

1. Oxidation progresses in four stages, principally by solution of oxygen, internal oxidation, film formation and by gas-oxide reactions.

2. The four oxidation stages were found to be time, temperature and pressure dependent.

3. Reaction rates which could be attributed wholly to solution of oxygen occurred at oxygen pressures of .03 microns.

While no evidence that oxidation proceeded beyond the solution stage was detected in any of the Cb samples exposed in InFab it becomes more certain that no such oxidation occurred in the samples of the third series of Cb samples exposed in the argon of highest purity level. This argument is supplemented by weight gain data which is compared in Figure 17 with weight gain data obtained by Inouye.

From the comparison graph in Figure 17 showing less weight gain for InFab exposed samples and from the test results discussed, it becomes evident that the kinetics of contamination by oxygen in argon greatly differs from that in vacuum. The data generated in this investigation also lends merit to Inouye's postulation that "exposure of metals to mixtures of gases would result in significantly different reaction rates due to competition of the individual gas species for the adsorption sites."

Inouye's postulation was founded upon the evidence he obtained by first exposing Cb samples in vacuum where the total residual gas was 0.1 microns of oxygen and secondly where the

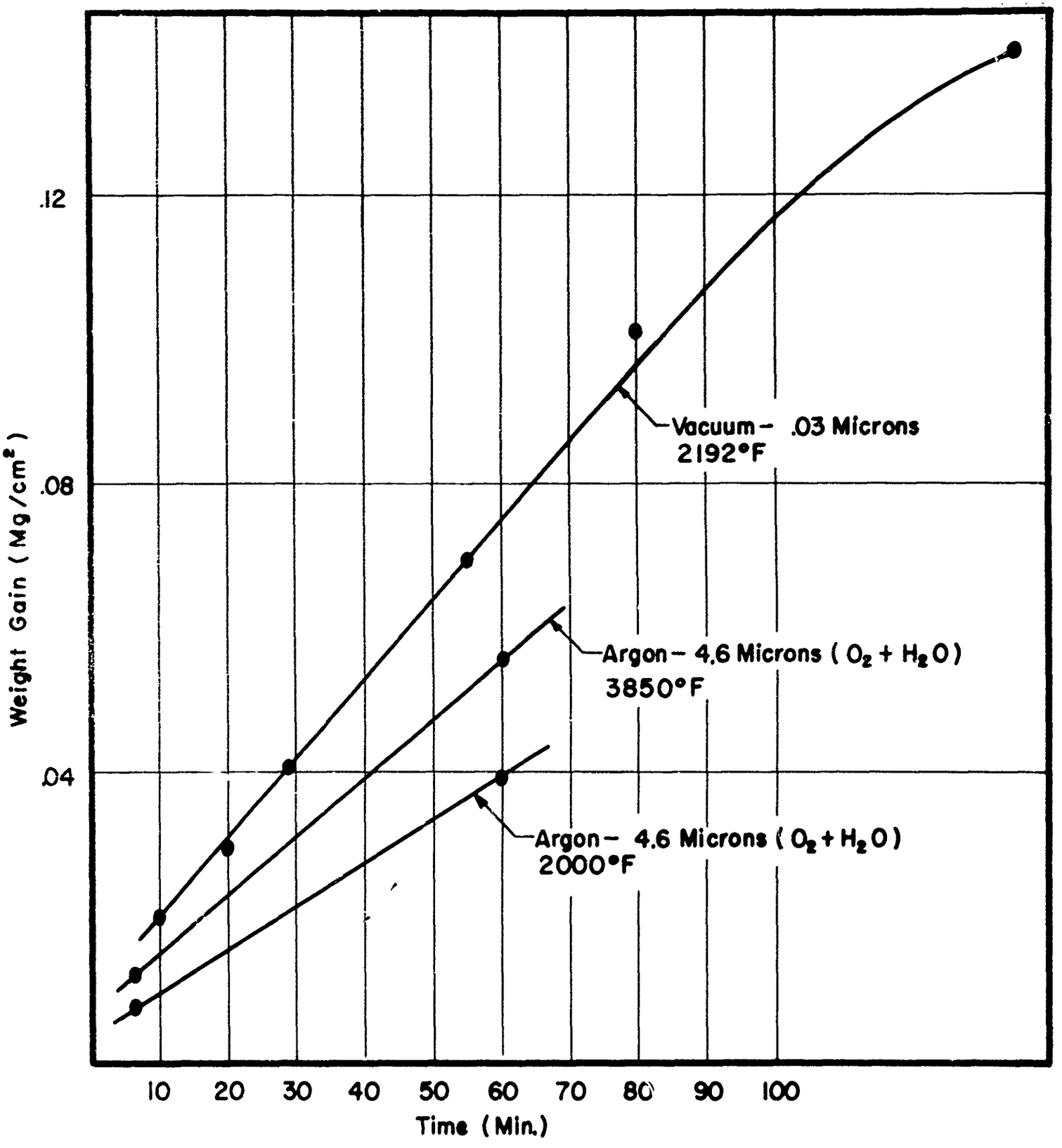


FIGURE 17

RATE OF OXYGEN SOLUTION IN COLUMBIUM
VACUUM VS INFAB ATMOSPHERE

RT-A-0592
6/24/64

residual gas was air at a pressure of 0.5 microns. The plotted weight gains resulting from this experiment as shown in Figure 18 indicate that the contaminating tendency of oxygen was detered by other air components. It was of interest to note that a comparison point representing the weight gain of a Cb sample exposed in InFab argon containing 1.2 ppm O_2 and 4.6 ppm H_2O fell slightly below the weight gain curve for a vacuum of 0.5 microns of air.

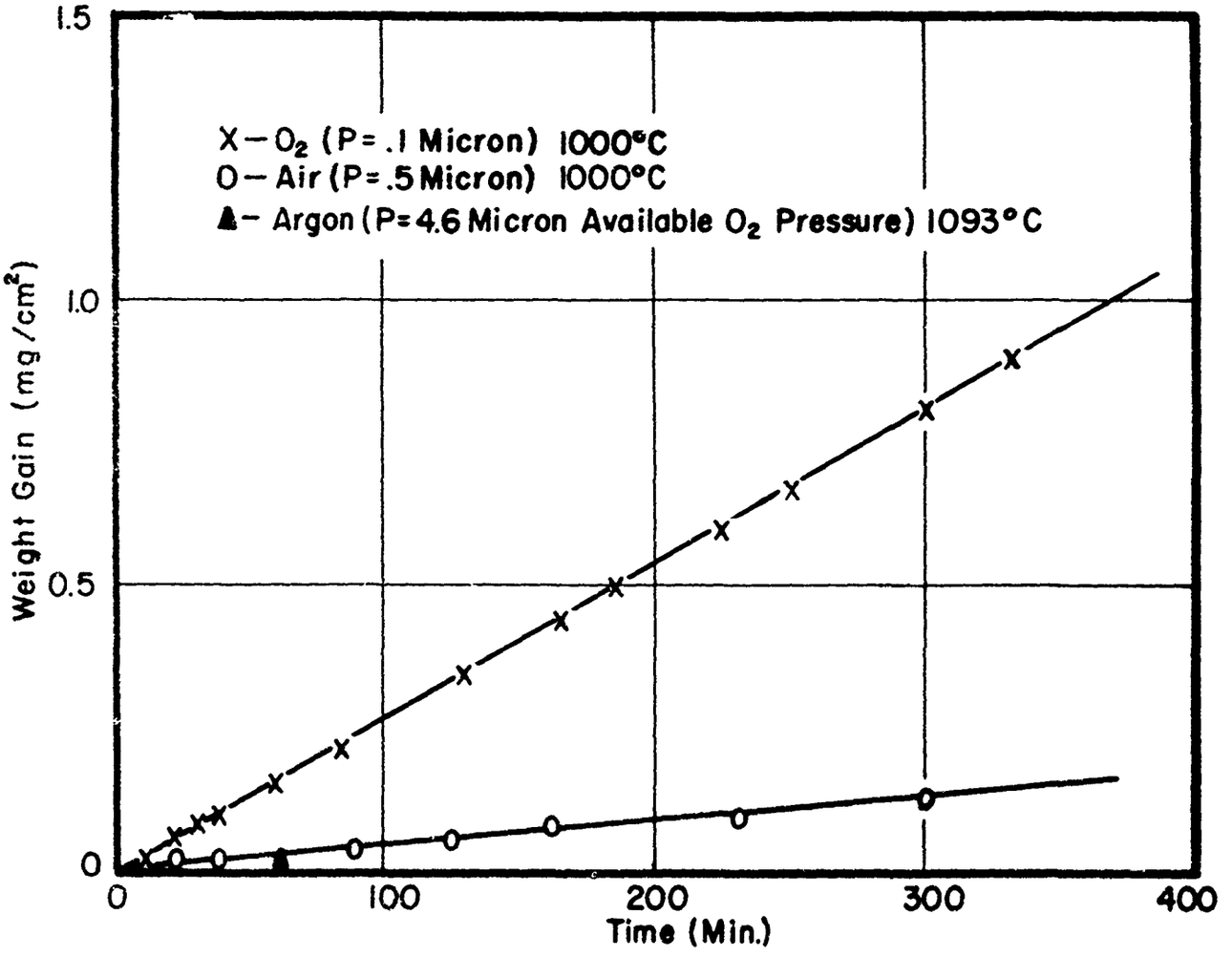


FIGURE 18

THE RATE OF CONTAMINATION OF COLUMBIUM AT INDICATED TEMPERATURES AND PARTIAL PRESSURES OF CONTAMINANTS

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References

1. Kofstad, P. and Krudtaa, O. J., Journal Less Common Metals 5 (1963) 477-492

2. Inouye, H. - "The Oxidation of Columbium at Low Oxygen Pressures" Cb Met Symposium AIME - June 1960