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HYDROGEN HALIDE CLEANING OF NICKEL-20 CHROMIUM CONTAINING DISPERSED THORIA

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ABSTRACT

The Cr_2O_3 content of powder metallurgy nickel-20 chromium-3 thoria was reduced with atmospheres consisting of hydrogen plus hydrogen chloride (HCl) or hydrogen bromide (HBr). The non-thoria oxygen content or "oxygen excess" was reduced from an initial amount of greater than 50,000 ppm to less than 100 ppm. Low temperatures were effective, but the lowest oxygen levels were achieved with the highest cleaning temperature - 1200°C.

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SUMMARY

This investigation was conducted to determine the effect of hydrogen halide additions to hydrogen on the reduction of Cr_2O_3 in powder metallurgy nickel-20 chromium-3 thoria. This material was prepared by attritor grinding in distilled water. After drying and hydrogen pre-cleaning, the powder was cold pressed and cleaned in hydrogen plus hydrogen chloride (HCl) or hydrogen bromide (HBr). Treatment temperatures ranged from 650°C to 1200°C. All cleaning treatments were followed by sintering in dry hydrogen at 1200°C. The hydrogen halides were effective in reducing the Cr_2O_3 content. The non-thoria oxygen content or "oxygen excess" was reduced from greater than 50,000 ppm to less than 100 ppm. The hydrogen halides were effective at low temperatures in reducing the Cr_2O_3, however, the lowest oxygen levels were achieved at the highest temperature - 1200°C. Carbon contents in the treated materials were also reduced to a level below that normally associated with the reaction of carbon with the excess oxygen present in the powder compacts.

INTRODUCTION

The successful processing of dispersion-strengthened materials requires that contamination be held to a minimum. (1) Matrix oxides are serious contaminants. And they must be reduced or eliminated if materials with thermally-stable microstructures are to be produced. Metal oxides that have a relatively small negative free energy of formation, i.e., CuO, CoO, and NiO, are easy to reduce at low temperatures with hydrogen. The reduction of chromium oxide (Cr_2O_3) is much more difficult. Reducing agents that have been used for Cr_2O_3 include hydrogen at high temperatures, carbon and hydrocarbon vapors, reactive metals, and halide vapors. Each approach to reduction has potential drawbacks. High temperatures can cause agglomeration of the added oxide; carbon and hydrocarbons can lead to carbon contamination. Reactive metals can leave a residue of impurity oxide. The halide vapors are toxic, corrosive, and may reduce the added oxide dispersoid. Despite the disadvantages of the halides, they offer a potential for reducing chromium oxide at low temperatures. And with the proper control, only the Cr_2O_3 and not the ThO_2 should be reduced.

The usefulness of hydrogen chloride (HCl) in reducing chromium oxide has been predicted from thermodynamic considerations by Maier (2) and Kellog (3), and verified experimentally by Maier (2). The reaction of HCl with Cr_2O_3 results in the formation of chromium chloride and water, viz,

$$1/3 \ Cr_2O_3 + 2HCl \longrightarrow 2/3 \ CrCl_3 + H_2O$$
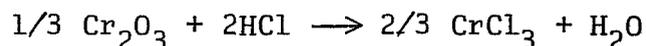
The free energy of this reaction is positive indicating that it is not spontaneous to the right. However, by continuously removing the water vapor formed by means of a dynamic gaseous atmosphere it is possible to keep the activity of the gases at less than unity. And thus make it possible for the reaction to take place. Diluting the HCl with hydrogen makes the atmosphere less corrosive and in addition a low dew point hydrogen helps in the reduction of the Cr_2O_3. After converting the Cr_2O_3 to $CrCl_3$, pure chromium can be obtained by removing the HCl from the system. Thus in the absence of water vapor, the following reaction will occur:

$$CrCl_3 + 3/2H_2 \longrightarrow Cr + 3HCl$$
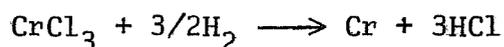
Based on chemical reactivity, hydrogen bromide (HBr) should also be effective. From thermodynamic and kinetic considerations it would seem desirable to carry out the reaction with the halide vapors at the highest possible temperature. As temperature is increased the moisture tolerance for reduction is increased and the reaction rate is increased. There is, however, a complicating factor. At a temperature of $815^{\circ}C$ chromium chloride becomes a liquid. And at $842^{\circ}C$ chromium bromide becomes a liquid. The presence of a liquid halide could tend to block the pores in a powder compact and essentially stop the cleaning reaction from penetrating to the center of a specimen. Further, the presence of a liquid could lead to liquid phase sintering which could alter the distribution of any added oxide phase.

Because of the above potential complications and because it is known that the intentionally added oxides (thoria in this case) tend to agglomerate when high sintering temperatures are used, preliminary experiments were conducted. The purpose of these preliminary experiments was to gain an insight into the quantity of HCl and HBr to be added to the hydrogen and to determine the range of cleaning temperatures to be investigated in detail.

The objective of this investigation was to determine the effect of hydrogen halide additions to hydrogen on the reduction of Cr_2O_3 in powder metallurgy nickel-20 chromium-3 thoria. Attritor ground nickel-20 chromium with 3 weight percent (W/O) thoria (ThO_2) was compacted and cleaned in hydrogen with either HCl or HBr additions. Most of the experiments involved isothermal exposure to atmospheres containing 2 volume percent (V/O) of the hydrogen halides in hydrogen. As mentioned previously, some preliminary experiments were also carried out. The preliminary experiments utilized 5V/O hydrogen halide

additions and a step heating cycle from 430°C to 1200°C. For the experiments with 2V/O hydrogen halide additions, the reaction temperatures were 650°, 930°, and 1200°C. And the cleaning times ranged from 4 to 24 hours. All cleaning treatments were followed by sintering in dry hydrogen at 1200°C. Evaluation of the effectiveness of reduction was obtained by the use of chemical analyses and both light and electron microscopy. A total of 13 experiments were carried out.

MATERIALS APPARATUS AND PROCEDURE

Powder Preparation

Nickel-20 chromium-3 thoria was prepared by the NASA comminution and blend technique (NAS-CAB). This technique developed by M. Quatinetz and J. W. Weeton has been described previously (4, 5). The attritor grinding pot was made of Nichrome and the grinding balls and stirrer were made of nickel. The grinding fluid was distilled water. No grinding aids were used. As shown by A. Arias (6), grinding under such conditions is known to oxidize the freshly cleaved surface of the powder. Thus the ground powder would contain a large quantity of oxygen. And the removal of this oxygen would be a good test of the effectiveness of any reduction treatments. The starting materials were minus 325 mech (44 μM) Continental Ore nickel-20 chromium powder and Thorium Limited colloidal (0.005 to 0.015 μM) thoria.

The ground powder was washed with distilled water and the supernatant liquid was removed by decantation. The resulting powder slurry was vacuum dried at ambient temperature. During drying, the slurry formed into a powder cake which was broken up by passing through a 40 mesh (420 μM) sieve. After sieving, the powder was loaded into a retort and given a preliminary cleaning and annealing treatment in flowing dry hydrogen at 800°C. Heating to the reaction temperature was controlled by the moisture evolution. In this operation, the effluent moisture level was kept below 200 ppm during heating. The retort containing the powder was transferred to an argon filled dry box. After removing the powder from the retort, compacts were made. For the preliminary experiments the compacts were spherical in shape and approximately 1/4 inch (0.64 cm) in diameter. These spherical compacts weighing about 0.2 grams each were prepared by hydropressing at 70 ksi (480 MN/M^2). For the bulk of the experiments cylindrical compacts were used. These were prepared in a 1/2 inch (1.27 cm) double acting die, at a compacting pressure of 150 ksi (1030 MN/M^2). The nominal powder weight was 2 grams. And the resulting thickness was about 1/4 inch (0.64 cm). The green density of these compacts was 58 percent of theoretical.

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Cleaning and Sintering Experiments

Cleaning and sintering experiments were conducted in "Globar" heated horizontal hot-wall tube furnaces. Furnace tubes and radiation shields were made of type 316 L stainless steel. The tubes were protected from catastrophic oxidation on the outside surface at elevated temperatures by using a flowing argon blanket. Hydrogen, dried to a level of less than 1 ppm H_2O, and anhydrous high purity HCl or HBr were metered through precision (one percent accuracy) flow meters and introduced into the furnace. The moisture level of the gas mixtures was in the range of 0.5 ppm (as measured by a gold-aluminum oxide capacitance type hygrometer). A schematic representation of the experimental apparatus is shown in Figure 1.

In all of the experiments, the compacts were loaded into tungsten boats and placed into the central zone of the furnace at room temperature. The uniformity of the hot zone at the reaction temperatures was determined to be $\pm$ 2°C. During the loading operation a constant flow of helium passed through the furnace. After closing the furnace, all seals were pressure checked for leaks. The helium flow was then turned off and the hydrogen flow simultaneously started. When the moisture level of the effluent hydrogen was equal to that of the affluent (0.5 ppm), the heating cycle was started. In the preliminary experiments, 10 spherical compacts were used. Five of the compacts were nickel-20 chromium, and 5 were nickel-20 chromium-3 thoria. A manually adjusted step heating schedule was used for these preliminary experiments. The samples were heated slowly to 760°C in dry hydrogen, cooled to 430°C and then the hydrogen halide (5 V/O) was added. After 20 hours at 430°C the hydrogen halide flow was turned off and the temperature increased by 100°C. The hydrogen halide was then turned on again for 20 hours. The last two steps were repeated until a temperature of 1200°C was reached. At 1200°C the hydrogen halide flow was for 10 hours followed by 10 hours in hydrogen alone. For most of the cleaning experiments, isothermal reaction treatments in hydrogen-2 V/O hydrogen halide were used. Three cylindrical compacts were used for each of the isothermal treatments. The heating was programmed with a curve follower type programmer. Heating from ambient to the isothermal reaction temperature was at a rate of 100°C per day in hydrogen. Once the isothermal reaction temperature was reached, the hydrogen halide (HCl or HBr) was added to the flowing hydrogen and the mixture was allowed to flow into the furnace for the desired reaction time interval (4 to 24 hours). Following the hydrogen halide treatment, the temperature was again increased in hydrogen at a rate of 100°C per day to the sintering temperature of 1200°C. A continuous record of temperature and effluent moisture level was made for each furnace run. A summary of the cleaning treatments used is shown in Table I. At the completion of the sintering step the furnace power was turned off and the furnaces allowed to cool to room temperature in a hydrogen atmosphere. The gas flow was then switched back to helium. After purging, the furnaces were opened and the samples removed.

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A total of 13 isothermal cleaning runs were carried out. Run 1 was in dry hydrogen at 1200°C for 20 hours. This was to serve as a standard for comparison of the effect of the hydrogen halide treatments. Runs 2-9 were in hydrogen-2 V/O HCl, and Runs 10-12 were in hydrogen-2 V/O HBr. A single experiment with a commercial nickel-20 chromium-2 thoria material (Fansteel TD NiCr- Run 13 in hydrogen-2 V/O HBr) was conducted to determine if a hydrogen halide treatment could be effective with a fully dense material. Specifically, could such a treatment remove the residual Cr_2O_3 known to be in the body of the material? This sample was not given the long time treatment typical of the low density compacts. Rather it was heated to 1200°C in about 4 hours in a hydrogen atmosphere. This was then followed by 24 hours in hydrogen-2 V/O HBr and a 24 hour hydrogen sinter, all at 1200°C.

All of the treated materials were analyzed for changes in chemical composition and examined by both light and electron microscopy.

RESULTS AND DISCUSSION

Preliminary Cleaning Experiments

Preliminary experiments with small hydropressed balls of water ground nickel-20 chromium and nickel-20 chromium-3 thoria established that hydrogen with 5 V/O of either HCl or HBr could be used to effectively reduce the Cr_2O_3 content. Chemical analyses of these materials after the step heating hydrogen halide treatment indicated the oxygen content of the non-thoriated materials was less than 50 ppm. Furthermore, no evidence of a liquid phase was evident although the highest temperature exposure with the hydrogen halide was considerably in excess of that for the formation of the liquid chromium halides. The treated materials did, however, contain an appreciable amount of porosity. This porosity is associated with the reduction of the high initial Cr_2O_3 content of the starting material ground in water. In removing the more than 5 W/O oxygen from the compacts, a large amount of residual porosity was left behind. Although these pores were present, the areas between them were dense. In these dense areas, the matrix was obviously very clean, and only a very small amount of residue oxide, presumably Cr_2O_3 was present. The porosity in the materials containing thoria was more pronounced, however, again there were dense areas. A typical structure of a dense area in a sample with thoria is shown in Figure 2. The particle size of the thoria in this material is 0.1 to 0.4 μM.

Although the preliminary results with the 5 V/O hydrogen halide appeared promising, there was a relatively serious drawback. The high percentage of hydrogen halide in the atmosphere was very corrosive to the hardware used in the thermal treatments. To alleviate this problem, the hydrogen halide level was reduced to 2 V/O. Most of the experiments described in this report were carried out with the hydrogen-2 V/O hydrogen halide atmospheres.

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Principal Cleaning Experiments

Reducing the hydrogen halide concentration to 2 V/O greatly reduced the corrosive attack on the furnace hardware. And the 2 V/O level was still effective in reducing the impurity Cr_2O_3 content of the powder metallurgy nickel-20 chromium-3 thoria. The most important analytical tool used for determining the effectiveness of a cleaning treatment is chemical analysis, consequently all treated materials were analyzed for changes in chemical composition.

The most direct evaluation of the effect of a cleaning treatment is the oxygen content of the treated material; specifically the oxygen greater than that stoichiometrically associated with any added oxide dispersoid such as ThO_2. This residue or impurity oxide has been given the term "oxygen excess". To determine "oxygen excess" we need the analysis for total oxygen content and the ThO_2 content of the material. To assure the reliability of the reported values for total oxygen, at least three determinations were made for each thermal treatment. As shown in the Appendix, the analysis for ThO_2 is quite complicated and requires a relatively large sample. For these reasons only one ThO_2 determination was carried out for each thermal treatment. All analyses for other metallic constituents were also single determinations. However, the carbon contents are based on three determinations.

Oxygen Analysis - From Table I it can be seen that treatment for 20 hours at 1200°C in dry hydrogen (Run 1) greatly reduced the oxygen level (from greater than 5 W/O to 6200 ppm). The resulting "oxygen excess" was 2800 ppm, presumably present in the form of Cr_2O_3. The effect of the hydrogen 2 V/O HCl treatment was shown by the fact that after only 9 hours at 930°C (Run 4) the "oxygen excess" was 2880 ppm. Increasing the exposure time and increasing the treatment temperature further reduced the "oxygen excess". After 24 hours at 1200°C in hydrogen-2 V/O HCl (Run 9) the analyzed oxygen content was less than enough to tie up the thorium. And the oxygen excess was indicated to be a minus 24 ppm. In view of the accuracy limitations of the thoria analysis (± 0.1 W/O - see Appendix), this value for "oxygen excess" can be considered to be less than 100 ppm.

Since it was apparent that higher reaction temperatures produced lower oxygen contents with the hydrogen-2 V/O HCl atmosphere, hydrogen-2 V/O HBr was evaluated only at the highest temperature - 1200°C. The oxygen level was again reduced. And the "oxygen excess" after treatment of 24 hours in hydrogen-2 V/O HBr (Run 12) was "minus 100 ppm". As mentioned previously, within the accuracy of the chemical analyses, this can be considered to be less than 100 ppm.

The NiCr treated for 24 hours at 1200°C in hydrogen 2 V/O HBr (Run 13) was reduced in oxygen content by only 270 ppm. The residual oxygen ("oxygen excess") of 2330 ppm suggests that a material which is 100 percent dense at the beginning of the cleaning operations is not well cleaned by the hydrogen-2 V/O HBr atmosphere. As will be shown later, the edge appeared cleaned of oxygen, but the cleaning reaction did not penetrate to the interior portions of the material.

Chromium Analysis - Analysis of the chromium content of the samples was done to see if the hydrogen halide reduction of Cr_2O_3 would alter the chromium content. As noted in Table I, the chromium content of the starting powder was 22.0 W/O. Adding 3 W/O of ThO_2 to the nickel chromium powder would lower the chromium content to 21.3 W/O. The hydrogen treated sample (Run 1) contained less than this amount (20.3 W/O). It can be assumed, however, that the difference between 21.3 and 20.3 W/O was due to the pick up of nickel from the grinding operation. This same nickel pick up also accounts for the lowering of the thoria content from the added amount of 3 W/O ThO_2 to the 2.8 W/O found in the hydrogen treated sample. The low (18.5 W/O) chromium content of the ground and pre-cleaned powder is due to the high analyzed oxygen level - greater than 5 W/O. (The actual oxygen content of the sample containing 18.5 W/O chromium would have to be 9 W/O to give a true chromium content of 20.3 W/O.) The various hydrogen halide treatments had little, if any, effect on the chromium content. The chromium analyses of the treated compacts was from 20.1 to 20.5 W/O. And for the TD Nichrome it was 20.0 W/O both before and after the hydrogen halide treatment.

Carbon Analysis - In all of the treated materials we find a very appreciable reduction in the carbon content. The starting compacts contained 760 ppm carbon. This was reduced to 135 ppm by treatment with hydrogen at 1200°C. (Run 1.) This reduction should be expected since a high temperature treatment of any high oxygen content material in a neutral or reducing atmosphere usually reduces the carbon content. Specifically carbon reacts with the excess oxygen to give CO or CO_2. It is also possible that when the heating is done in hydrogen some methane (CH_4) would be formed. The further reduction in the carbon content after treatment in the hydrogen halide atmospheres is shown in Table I. Treatments at 650°C in hydrogen-2 V/O HCl (Runs 2 and 3) reduced the carbon level to about 90 ppm. At 930°C (Run 5) the carbon content was 33 ppm. All of the samples treated in hydrogen halide atmospheres at 1200°C exhibited carbon levels of 20 ppm or less. This includes the sample of TD NiCr which was reduced in carbon content from 196 ppm to 15 ppm.

Iron Analysis - During the analysis for the thoria content of the treated materials, the analytical chemist noted an iron residue. Since only a minor amount of iron was present in the starting materials this was not expected. As can be seen In Table I, the amount of iron generally increased with the time and temperature of the hydrogen halide treatments. Also higher iron levels were observed with the HBr treated samples. The maximum iron level (10.1 W/O) was in a sample treated for 16 hours at 1200°C in hydrogen-2 V/O HBr (Run 11). Since the chromium and thoria content was apparently not affected by the iron pick up, it was concluded that other losses from the compacts, i.e., nickel, must be compensating for the increase in iron. However, since the iron contamination was traced to the furnace tubes and radiation shields, it will be eliminated from future work by using nickel lined tubes and nickel radiation shields.

MICROSTRUCTURE

Photomicrographs at 1000X of random areas of the materials receiving 9 hour hydrogen plus hydrogen halide treatments are shown in Figure 3. The general structure shown is typical of low density compacted and sintered powder-metallurgy materials. At 650°C the porosity is highly angular and interconnected. When the temperature was increased to 930°C the porosity became less, but was more rounded, slightly larger in size, and less interconnected. At 1200°C the pores again increased in size, decreased in number and became less interconnected. There was also a noticeable increase in density of the structure following the 1200°C treatments. In comparing the HCl and HBr treatments we find that the HBr produces a slightly more porous structure, otherwise the materials are quite similar. Very little edge effect was noted in any of the materials since the reducing gases could readily penetrate to the center of the compacts. Figure 4 at 100X shows the type of pore distribution obtained for all of the materials treated at 650°C, 930°C, and for the materials treated for 4, 9 and 16 hours at 1200°C. When the time at 1200°C was increased to 24 hours a densification of the edge became apparent, Figure 5. When examining the materials at higher magnification it was found that they were too porous to permit satisfactory preparation for electron microscopic examination. Each sample was examined with the electron microscope, but no electron micrographs of the "as treated" materials were made. In order to see if the thoria were uniformly distributed in the materials, the sample cleaned for 4 hours at 1200°C in hydrogen-2 V/O HCl (Run 6) was subsequently hot pressed. The pressing was done in air at 250°C and 100 ksi (690 MN/M^2). The density increase in the sample is shown in the before and after 1000X microstructures shown in Figure 6. An electron micrograph of a typical area of the hot pressed sample is shown in Figure 7. The oxide particles ranged from 0.05 to 5.0 μM in size. The larger particles were assumed to be Cr_2O_3, and the smaller ones ThO_2. The smaller thoria particles ranged from 0.05 to 1.5 μM. A rough estimate of the amount of thoria present gives a value of 2 to 4 V/O. This is in good agreement with calculated value of 2.5 V/O which would be present in a nominal 3 W/O material.

The TD NiCr treated 24 hours at 1200°C in hydrogen 2 V/O HBr (Run 13) exhibited an edge effect. The 100X microstructure shown in Figure 8 shows the nature of this effect. The first 20 μM is quite clean. And presumably it represents either a chromium depletion zone or an area rich in iron deposited by the hydrogen-2 V/O HBr atmosphere. The next 40 μM contains relatively large isolated porosity. The interior portion of the specimen appears unaffected by the treatment.

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CONCLUDING REMARKS

The results of this study have indicated that hydrogen-halide atmospheres can be used to effect an appreciable reduction in the oxygen content of powder-metallurgy nickel-20 chromium-3 throia. Since Cr_2O_3 was the main contaminant removed, this treatment should also be applicable to other chromium containing alloys. Also although the greatest reduction occurred at the highest reaction temperature - $1200^{\circ}C$, considerable benefit was obtained at temperatures as low as $930^{\circ}C$. Presumably longer times at even lower temperatures could also be effective. And work along these lines should be pursued.

Much significance has been placed on the reduction in oxygen. The concurrent reduction in carbon level that was achieved is also important. Conceivably lower carbon contents might improve the stability of the material - particularly in terms of long time high temperature exposure.

SUMMARY OF RESULTS

An investigation carried out to determine the effect of hydrogen halide additions to hydrogen on the reduction of Cr_2O_3 in powder metallurgy nickel-20 chromium-3 thoria yielded the following results:

1. The addition of 2 V/O of HCl or HBr to hydrogen is an effective reducing atmosphere for Cr_2O_3. Impurity oxygen was reduced from greater than 50,000 ppm to a less than 100 ppm.

2. Low reaction temperatures (650° and $930^{\circ}C$) permit reduction to occur, but the lowest impurity oxygen levels were obtained at the highest reaction temperature - $1200^{\circ}C$.

3. Hydrogen alone at $1200^{\circ}C$ reduced the impurity oxygen appreciably, but not as completely as with the hydrogen halide additions.

4. The presence of the hydrogen halides also reduced the carbon level below that normally associated with the reaction of carbon with the excess oxygen present in the compacts.

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APPENDIX

ANNALYTICAL PROCEDURE FOR DETERMINATION OF THORIA (ThO_2) IN NICKEL-20 CHROMIUM-3 THROIA

The determination of thoria is based on the dissolution of the sample in aqua-regia. And the insoluble ThO_2 is removed by filtration.

1. Weigh 2 to 4 grams of sample and place in a 250 millilieter beaker.

2. Add 25 millilieters of HCl and 10 millilieters of HNO_3. Heat gently to dissolve, then bring solution to a boil.

3. Dilute to 200 millilieters with distilled water and heat on a low heat hot plate.

4. Add a little paper pulp to the sample solution and filter through a tight filter paper into a 500 millilieter volumetric flask.

5. Police the beaker and transfer, quantitatively, all the precipitate to the filter.

6. Wash the filter and precipitate six times with 1% HCl.

7. Place filter in a tared platinum crucible, dry, char the paper, then ignite in a muffle for two hours at 1000°C.

8. Cool in a desicator and weigh.

This procedure was used by W. A. Dupraw of the Chemical Analysis Unit of the Analytical Laboratories Section. And his assistance in the determination of the ThO_2 content of the samples used in this report is greatfully acknowledged. Based on Mr. Dupraw's experience with nickel-20 chromium-3 thoria it appears that an accuracy of $\pm$ 0.1 percent can be ascribed to the determination of ThO_2. Furthermore, the value obtained for the thoria content depends on the complete solution of the nickel-20 chromium. If complete solution were not achieved you would expect the analyzed ThO_2 content to be slightly high. This leads to a reasonable explanation for the negative values for "oxygen excess" obtained in some cases. The stoichiometric oxygen equivalent for 0.1 percent ThO_2 is 121 ppm. Thus, if the reported ThO_2 content is too high by 0.1 percent, an "oxygen excess" of minus 24 ppm becomes plus 97 ppm.

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TABLE I – TREATMENT SCHEDULE AND CHEMICAL ANALYSIS OF POWDER METALLURGY NICKEL-20 CHROMIUM-3 THORIA

RUN	TREATMENT[1]	CARBON PPM	OXYGEN PPM	ThO_2 %[2]	"OXYGEN EXCESS" (PPM)	IRON %	CHROMIUM %
	As received (no ThO_2)	750	1500	--	--	.32	22.0
	As ground, precleaned and pressed, ThO_2 added	760	>50000	2.6	>50000	.37	18.5
1	20 hours, 1200°C hydrogen	135	6200	2.8	2800	NA[3]	20.3
2	4 hours, 650°C hydrogen-2 V/O HCl	89	>10000	2.8	>6600	1.1	NA
3	9	90	9500	>1.9[4]	<7200[5]	NA	20.1
4	9 930°C	NA	6030	2.6	2880	1.5	NA
5	16	33	4870	2.7	1600	2.3	20.5
6	4 1200°C	20	4610	2.8	1220	0.9	NA
7	9	NA	3245	>2.2[4]	<580[5]	NA	NA
8	16	13	3740	2.6	590	5.0	NA
9	24	8	3370	2.8	-24	2.7	20.2
10	9 1200°C hydrogen-2 V/O HBr	NA	3380	>1.7[4]	<1320[5]	NA	NA
11	16	14	3800	>2.2[4]	<1130[5]	10.1	NA
12	24	NA	3290	2.8	-100	8.4	20.5
	As received TD Nichrome sheet	196	5020	2.0	2600	.006	20.0
13	24 hours 1200°C hydrogen-2 V/O HBr	15	4750	2.0	2330	1.7	20.0

Notes: 1. All cleaned materials sintered for 10 hours at 1200°C in hydrogen except those receiving a 24 hour hydrogen halide treatment. Materials treated in hydrogen halide for 24 hours were sintered for 24 hours.
2. Impurity oxygen.
3. Not analyzed.
4. Limited sample material prevented reliable analysis. The sample contained at least this much ThO_2.
5. "Oxygen excess" depends on ThO_2 analysis. If the ThO_2 analysis is lower than the actual thoria content, the "oxygen excess" will be high.

FIGURE 1 CLEANING APPARATUS(SCHEMATIC)

Argon

"Globar" Furnace

Thermocouples
(Pt-Pt 13 Rh)

Radiation
Shield

Boat

Moisture probe

H_2O

Moisture Probe

Flow
Meters

Two
Channel
Recorder

Power Supply
&
Temp. Control

To Vent

Programmer

ALL SOLID LINES ARE GASEOUS FLOW
ALL DASHED LINES ARE POWER AND INSTRUMENTATION

Hydrogen   Halogen
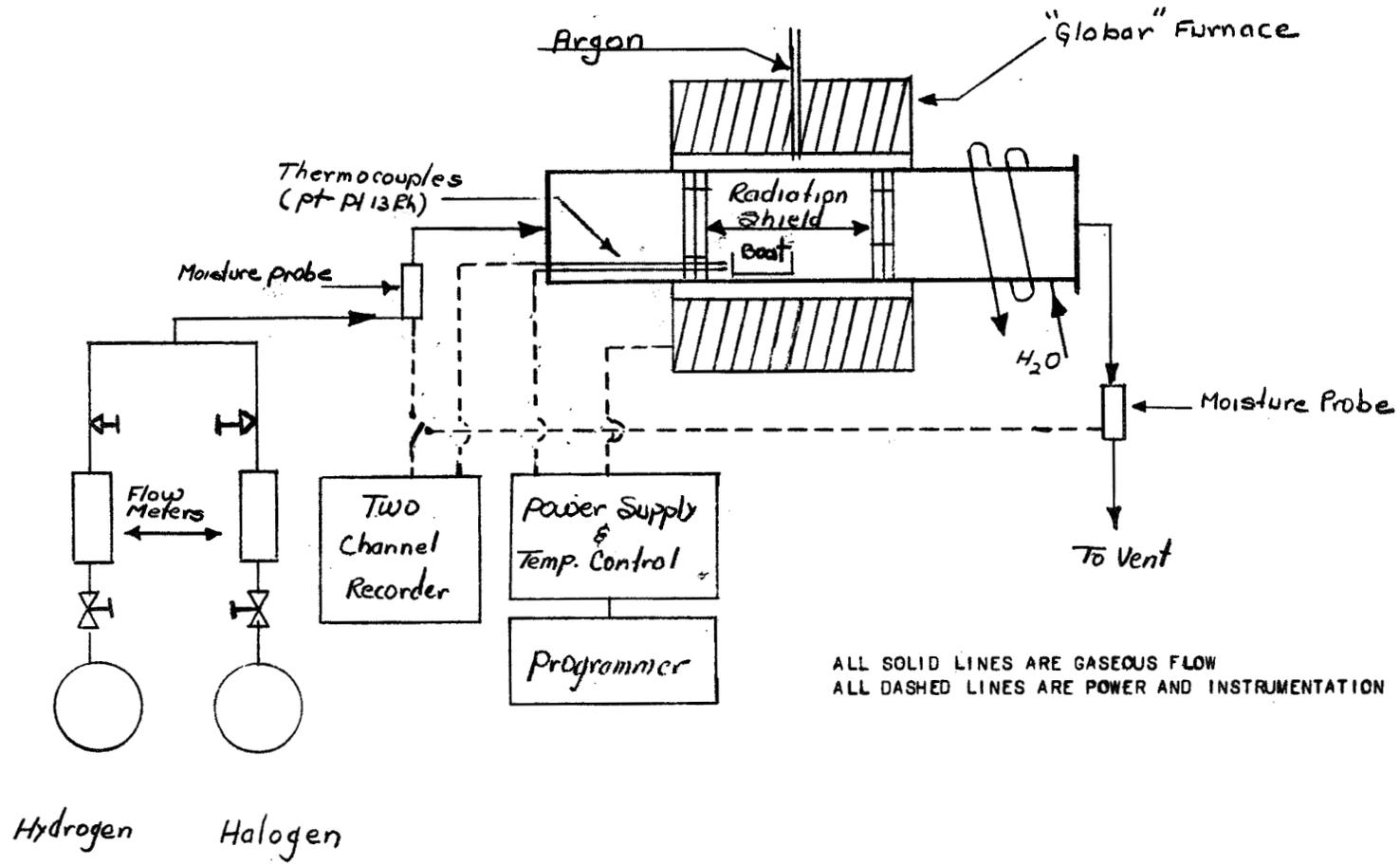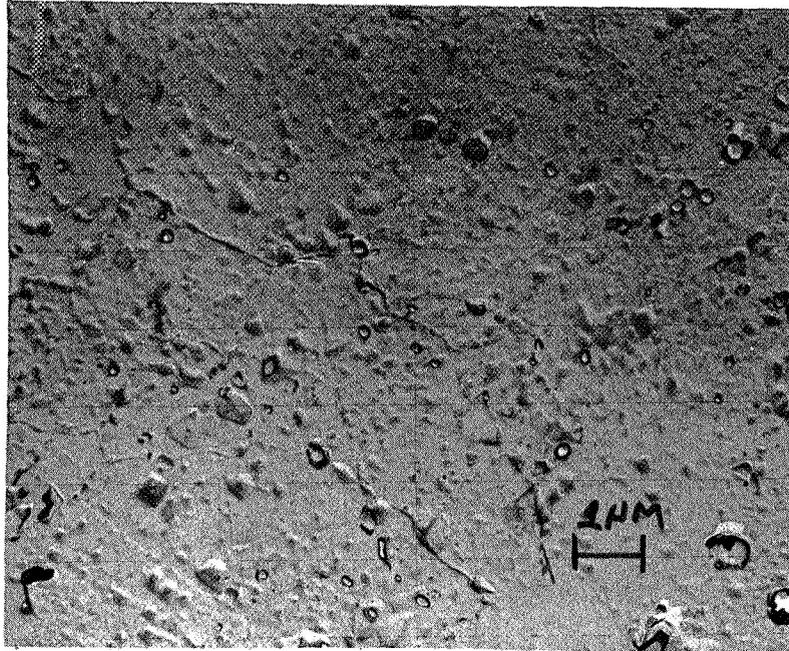
Figure 2. - Hydropressed ground   powder metallurgy
nickel-20 chromium-3 thoria step heating cycle to
1200°C in hydrogen-5V/O HCL.
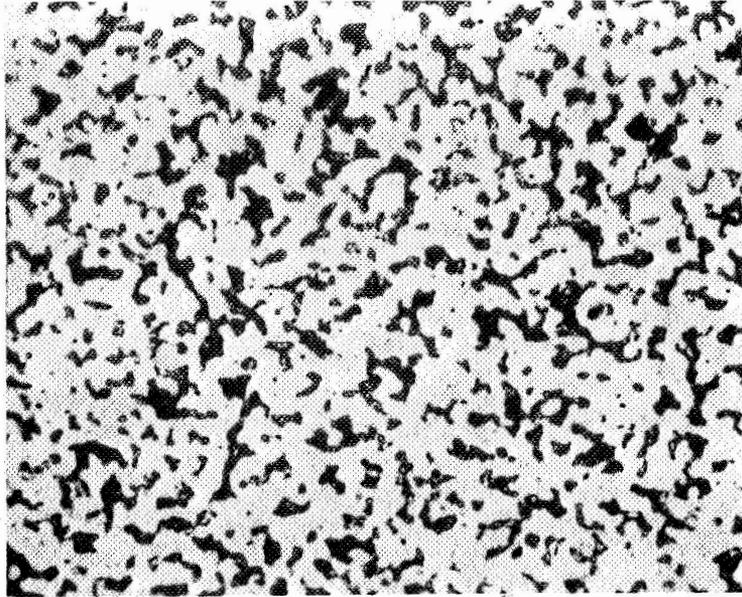
A. 2V/O HCL at 650°C (Run 3).
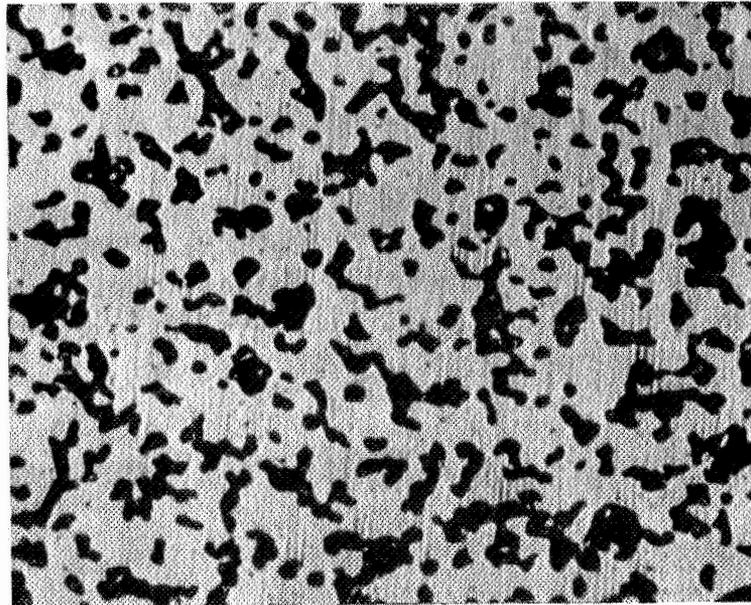
B. 2V/O HCL at 930°C (Run 4).

Figure 3. - Pressed cleaned and sintered   powder
metallurgy nickel-20 chromium-3 thoria treated 9
hours in hydrogen-2V/O HCL or HBR X1000, unetched.
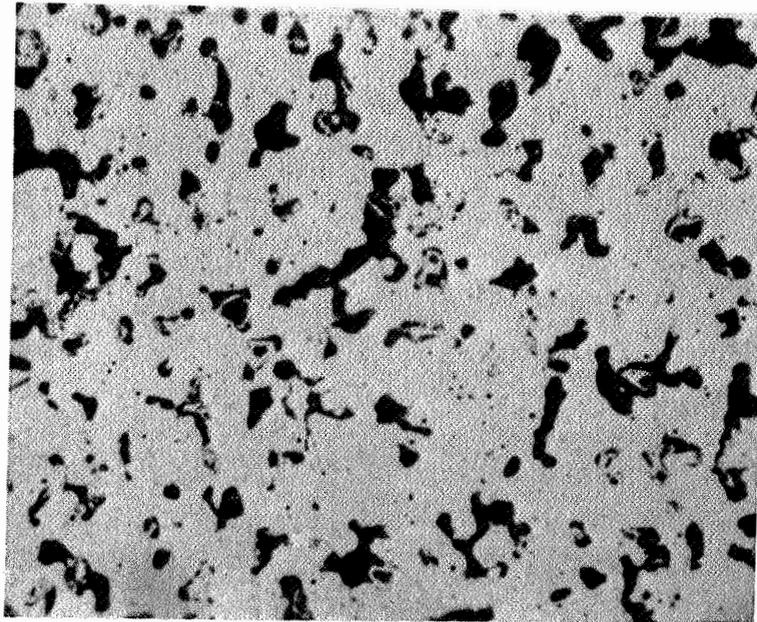
C. 2V/O HCL at 1200°C (Run 7).
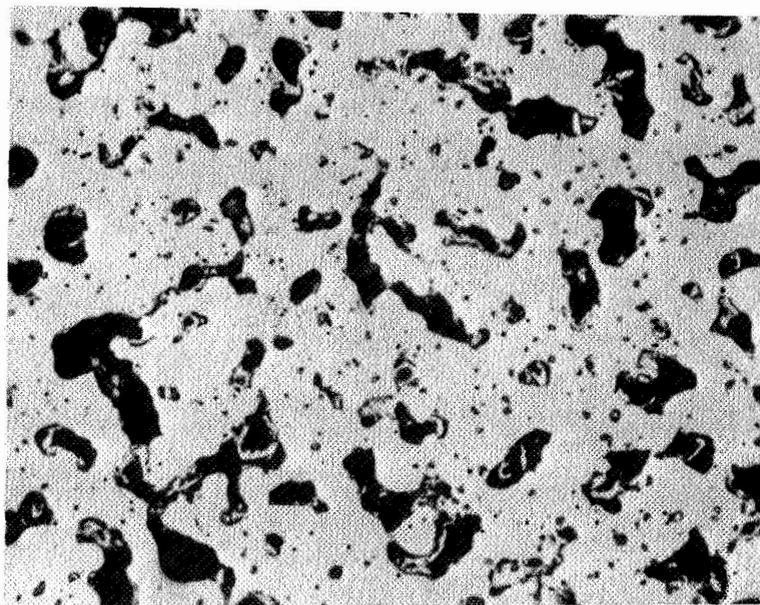
D. 2V/O HBR at 1200°C (Run 10).

Figure 3. - Continued.
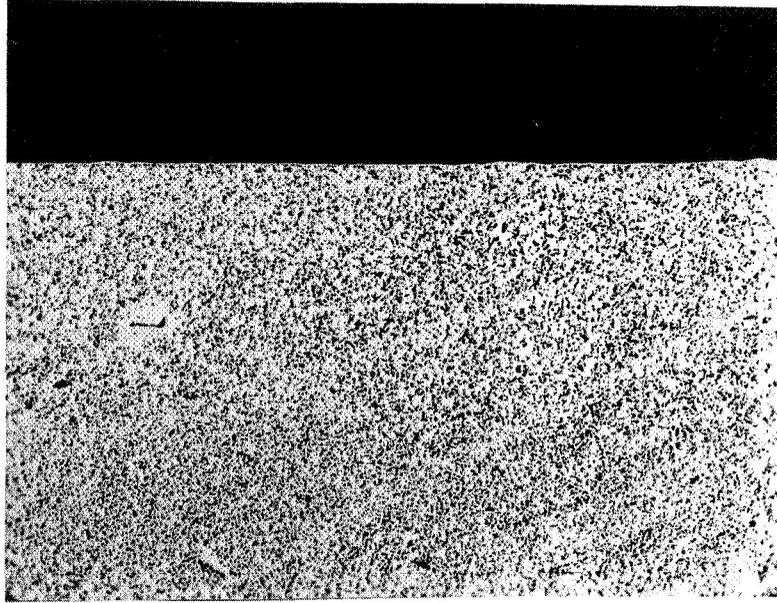
Figure 4. - Pressed cleaned and sintered   powder
  metallurgy nickel-20 chromium-3 thoria treated 16
  hours at 930°C in hydrogen-2V/O HCL (Run 5) show-
  ing absence of edge effect X100, unetched.
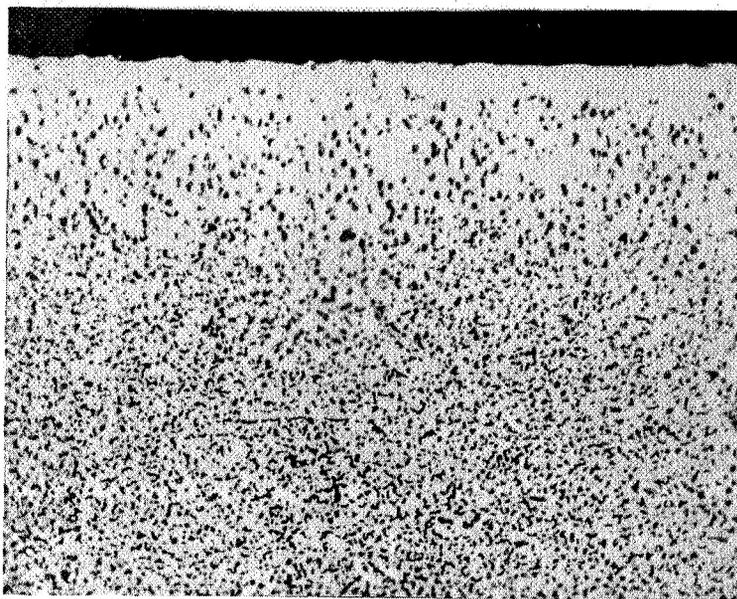
Figure 5. - Pressed cleaned and sintered   powder
metallurgy nickel-20 chromium-3 thoria treated 24
hours at 1200°C in hydrogen-2V/O HBR (Run 12)
showing edge effect X100, unetched.
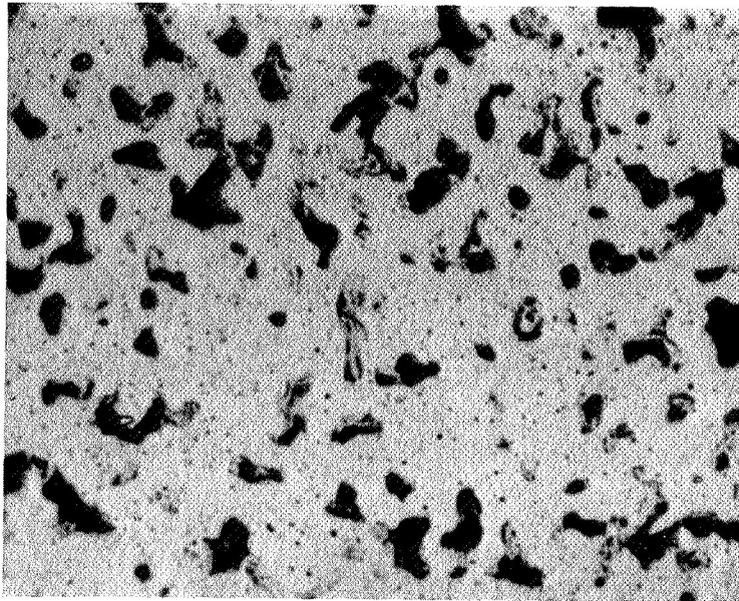
A. As treated.
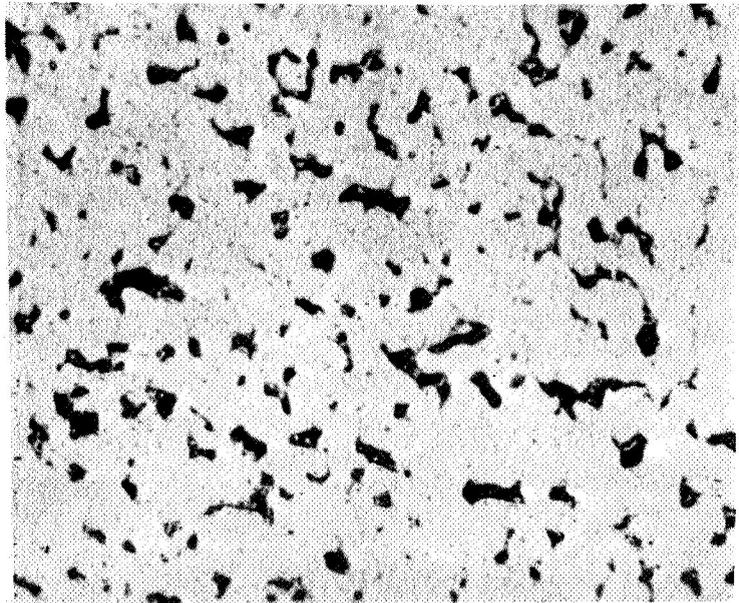
B. After hot pressing in air at 250°C.

Figure 6. - Pressed cleaned and sintered   powder
metallurgy nickel-20 chromium-3 thoria treated 4
hours at 1200°C in hydrogen-2V/O HCL (Run 6)
X1000, unetched.
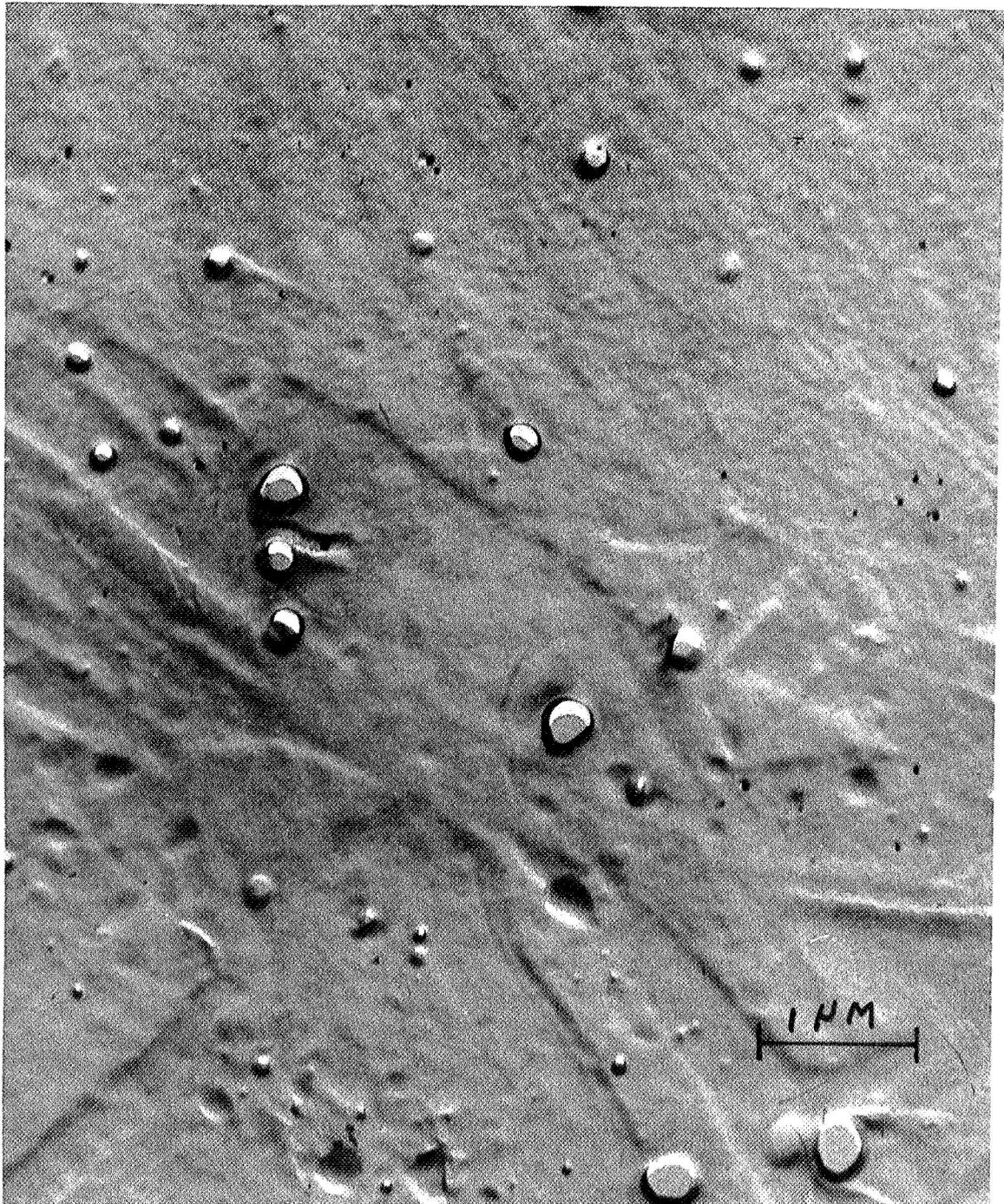
Figure 7. - Pressed cleaned and sintered powder
metallurgy nickel-20 chromium-3 thoria treated 4
hours at 1200°C in hydrogen-2V/O HCL (Run 6)
after hot pressing in air at 250°C.
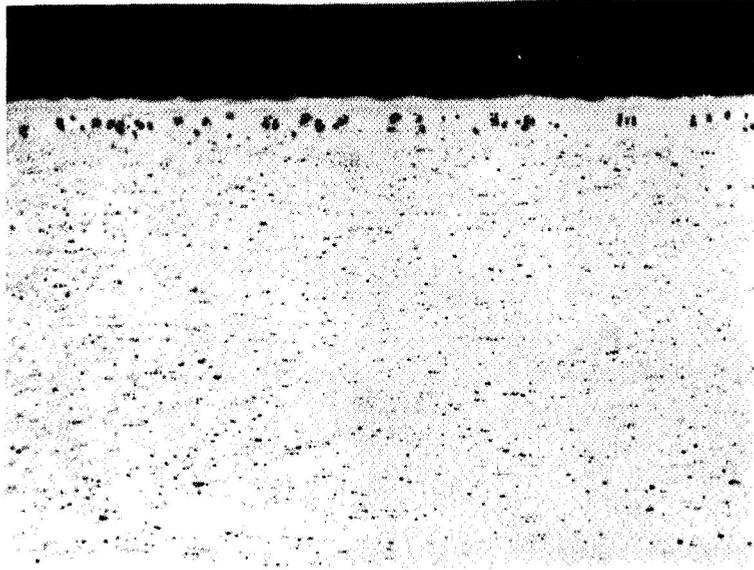
Figure 8. - TD NiCr treated 24 hours at 1200°C in
hydrogen-2V/O HBR (Run 13) showing edge effect
X100, unetched.