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RARE EARTH MODIFIED HIGH STRENGTH STEELS VIA P/M PROCESSING.(U)

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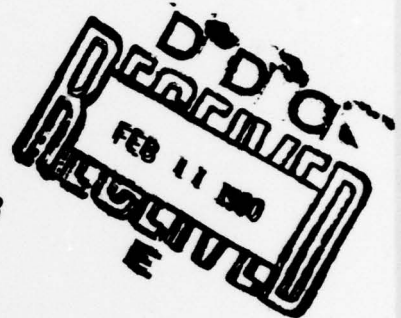
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TRW INC.

**RARE EARTH MODIFIED HIGH STRENGTH
STEELS VIA P/M PROCESSING**

By
A. A. SHEINKER



TECHNICAL REPORT

Prepared for
Office of Naval Research
Contract **N00014-74-C-0672**
NR 036-132

DECEMBER 1979

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ER-8097

TECHNICAL REPORT

**RARE EARTH MODIFIED HIGH STRENGTH STEELS VIA
P/M PROCESSING**

Prepared for

Office of Naval Research
Contract N00014-74-C-0672

December 1979

by

A. A. Sheinker

TRW Inc.
TRW Equipment
Materials Technology
Cleveland, Ohio 44117

FOREWORD

The work described in this report was performed in the Materials Technology Laboratory of TRW Inc., under the sponsorship of the Office of Naval Research, Contract N00014-78-C-0672. Dr. P. A. Clarkin acted as Program Monitor for the Navy. The program was administered for TRW by Dr. C. S. Kortovich, Program Manager. The Principal Investigator was Dr. A. A. Sheinker, with technical assistance provided by Mr. J. W. Sweeney and Mr. R. R. Ebert. The work conducted during the first year of this contract, covered in this report, involved studies of material processing techniques for producing rare earth modified 4340 steel from metal powders.

This report has been assigned TRW Equipment Number ER-8097 and the data are recorded in laboratory notebook Number 794.

ABSTRACT

Material processing studies were initiated directed toward developing powder metallurgy methods for producing rare earth modified high strength 4340 steel with improved resistance to hydrogen embrittlement. Three different methods of making rare earth modified 4340 steel powders were explored: hydrogen gas atomization, mechanical alloying, and rapid solidification rate atomization. These studies included metallographic characterization of powders made by all three of these methods and preliminary mechanical property evaluation of compacted material made from hydrogen gas atomized powder. Hydrogen gas atomization of 4340 steel prealloyed with cerium by adding a 75%Ce - 25%Ni alloy to the melt produced powder particles which were irregular in shape, clean, and relatively free of nonmetallic inclusions. The mechanical properties of this powder material consolidated by hot isostatic pressing (HIP) at 2000°F (1370°K) and heat treated were generally lower than those of similarly heat treated, rare earth modified, wrought 4340 steels evaluated previously, due to a brittle condition in the prior particle boundaries of the compacted material. Mechanical alloying of hydrogen gas atomized 4340 steel powder containing no rare earths with either 75%Ce - 25%Ni or LaNi₅ alloy powders by attriting in a special high-intensity ball mill showed that annealing of the steel powder prior to attriting was necessary in order for the attriting to be effective. Rapid solidification rate (RSR) atomization of a control heat of 4340 steel with no rare earth additions produced powder particles which were generally spherical in shape, clean, and relatively free of nonmetallic inclusions, but contained many internal voids. The solidification patterns on the RSR particle surfaces were generally dendritic, as compared with those on the surfaces of the hydrogen gas atomized powder particles which were equiaxed, but no differences in the microstructures of these two types of powders could be discerned by light microscopy.

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I. INTRODUCTION

Hydrogen embrittlement is one of the major factors that prevents the utilization of high strength steels to their full potential. This is because, for a given type of steel, the susceptibility to hydrogen embrittlement generally increases with increasing strength level, so that these steels cannot be processed to their highest possible strength levels for applications where hydrogen embrittlement is a potential problem (1-3). Hydrogen embrittlement in high strength steels typically results from the absorption of hydrogen by the metal during processing operations such as acid pickling, electroplating, and welding (4). The adverse effects of hydrogen embrittlement on the mechanical properties of high strength steels include reductions in tensile strength and ductility, increased notch sensitivity, and slow crack growth leading to delayed failure (5,6). Because of the general nature of hydrogen embrittlement, failures caused by this phenomenon have been encountered in such diverse engineering structures and components as aircraft landing gears, pressure vessels, pipelines, oil well casing, electrical generator rotors, springs and bolts.

Considerable effort has been devoted to developing methods of preventing hydrogen embrittlement in high strength steels because of the magnitude and extent of the problem. These methods include changes in microstructure (7), changes in alloy composition (7), baking (8), surface prestressing (9), plating (10), cathodic protection (11), nonmetallic coating (12), selective changes in surface composition by heat treatment (13), and modification of the embrittling environment (14). All of these approaches have serious limitations in practical applications, so that no truly satisfactory method has emerged. However, a new method which has considerable potential is the addition of rare earth elements to high strength steels.

Previous studies have shown that the rare earths, which are believed to interact with hydrogen, are effective in controlling hydrogen blister formation and preventing hydrogen-induced weld cracking in steels. For example, the addition of 0.2 weight percent cerium to 4340-type steels reduced the susceptibility to hydrogen blister or flake formation by forming stable hydrides below 1850°F (1010°C) (15). Combined additions of cerium and lanthanum (approximately 60 percent cerium and 40 percent lanthanum) at levels of 0.05, and 0.09, and 0.13 weight percent in HY-80 steel decreased the susceptibility of weldments of this alloy to hydrogen-induced cracking, with the maximum effect occurring at the 0.09 weight percent rare earth level (16,17). The addition of approximately 0.2 weight percent Misch metal (50 percent cerium, lanthanum, and small amounts of other rare earths) eliminated the hydrogen typical of that remaining in HY-30 steel weld metal made with an intentional 5 percent hydrogen contamination in the argon arc shielding gas (18).

The effects of rare earth additions on the hydrogen embrittlement cracking resistance of AISI 4340 steel were systematically evaluated at TRW Materials Technology under ONR Contract No. N00014-74-C-0365 (19). In the first phase of this study, the hydrogen embrittlement cracking resistance of vacuum-induction melted 4340 steel containing about 0.05, 0.1, and 0.2 weight percent cerium or lanthanum was determined. This material was heat treated to a yield strength level of approximately 205 ksi (1410 MPa) by austenitizing, quenching, and tempering at 450°F (505°K). The test specimens were cathodically charged

with hydrogen, plated with cadmium to contain the hydrogen in the metal, and baked at 300°F (420°K) to homogenize the hydrogen content. Sustained load delayed failure tests showed that, at the 0.2 weight percent rare earth level, the threshold stress intensity (i.e., the stress intensity level below which failure did not occur) increased by a factor of about four and the crack growth rate decreased by about an order of magnitude as compared with 4340 steel without rare earth additions. This improvement was attributed to the ability of the rare earth elements to interact with hydrogen, thereby reducing the supply of hydrogen available for embrittlement and impeding the diffusion of hydrogen to the crack tip where it would accumulate and cause crack growth by local embrittlement.

In the second phase of this program, the concept of rare earth additions to high strength steels was extended to stress corrosion cracking behavior, because this type of failure in high strength steels is believed to be a form of hydrogen embrittlement (20). Three heats of 4340 steel containing zero, 0.20, and 0.30 weight percent cerium were heat treated to a yield strength level of approximately 215 ksi (1480 MPa) by austenitizing, quenching, and tempering at 450°F (505°K), and their resistance to stress corrosion cracking in 3.5 percent sodium chloride solution at room temperature was evaluated. The cerium additions had a much smaller effect on the stress corrosion cracking resistance than the cerium and lanthanum addition had on the hydrogen embrittlement cracking resistance in the previous study. The stress corrosion cracking threshold (K_{Isc}) was about the same for all three steels, ranging from 15 to 17 ksi $\sqrt{\text{in.}}$ (16.5 to 19 MPa $\sqrt{\text{m}}$). The higher cerium (0.30%) material had longer failure times and lower average crack growth rates than the lower cerium (0.20%) material. The failure times and average crack growth rates for the steel without cerium could not be directly compared with those for the two cerium-bearing steels because of crack branching which occurred only in the material without cerium. However, it was estimated that in the absence of branching, the failure times for the non-cerium steel would be shorter and the average crack growth rates higher than those for the lower cerium steel. The difference between the effects of the rare earth additions on stress corrosion cracking and hydrogen embrittlement cracking was attributed to the difference in the source of hydrogen in the two cracking phenomena, which affects the amount of hydrogen available for embrittlement and the processes of hydrogen transport to the tip of the crack.

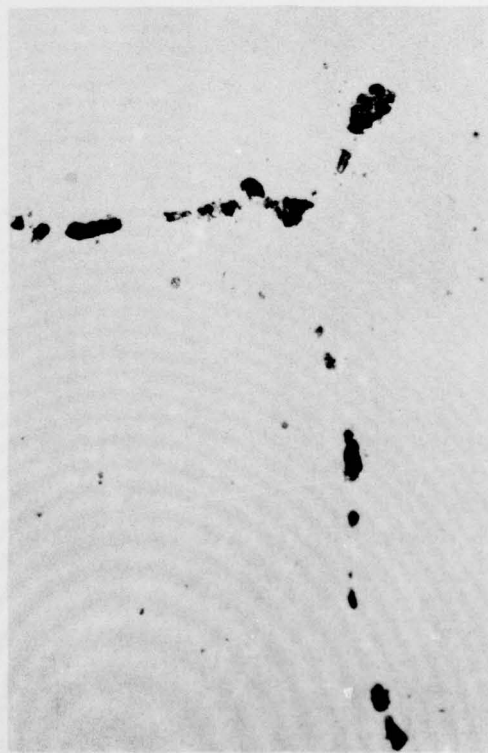
A major limitation in these experimentally prepared rare earth modified high strength steels was a degradation in mechanical properties with increasing rare earth content. The decreases in strength were small, but the reductions in ductility and impact resistance were substantial, on the order of 30 percent for percent elongation, 40 percent for percent reduction of area, and 50 percent for Charpy impact energy at the 0.2 weight percent rare earth level. This degradation was attributed to the presence of nearly continuous networks of rare earth oxide inclusions at the prior austenite grain boundaries, as shown in Figure 1. These inclusions were apparently formed as a result of the combination of the highly reactive rare earth elements with the residual oxygen in the vacuum induction melting atmosphere and were not dispersed by extensive hot working of the steel ingots. The segregation of the rare earths into these large inclusions was also suspected to have impaired their ability to interact with hydrogen and thus inhibit hydrogen embrittlement (21). In order to overcome this problem a method is required for incorporating the rare earth elements into the steel microstructure in a more homogeneous and uniform distribution.



a) - No Rare Earth Additions



b) - .033 w/o Cerium



c) - .092 w/o Cerium



d) - .170 w/o Cerium

Figure 1. Light photomicrographs of 4340 steel containing various amounts of cerium, unetched. Magnification, 500X.

The objective of the current program being conducted under ONR Contract N00014-78-C-0672 is to develop a powder metallurgy method for making rare earth modified high strength steels with improved resistance to hydrogen embrittlement. The powder metallurgy approach offers a means of obtaining a more uniform distribution of the rare earth elements in the steel and minimizing the formation of rare earth oxide inclusions. This should improve the ductility and impact resistance and also enhance the hydrogen embrittlement resistance of rare earth modified high strength steels. This report describes the work conducted during the first year of the program. This work involved the development of processing techniques for producing rare earth modified 4340 steel from metal powders.

II. PROGRAM OUTLINE

The objective of this program is the development of powder metallurgy methods for the production of rare earth modified high strength steels with improved resistance to hydrogen embrittlement. To accomplish this, work is being directed towards evaluating the applicability of various powder metallurgy processing techniques including appropriate canning methods for the production of rare earth modified 4340 steel powders. Current efforts involve a detailed study of these processing approaches, and a flow chart outlining this portion of the program is presented in Figure 2. Three different techniques for making the metal powders are being explored: hydrogen gas atomization, mechanical alloying, and rapid solidification rate atomization. These three methods were chosen because of their potential for producing a uniform distribution of the rare earth elements in the steel and minimizing the formation of rare earth oxide inclusions. The rare earth elements cerium and lanthanum were selected for this study on the basis of the previous work conducted at TRW which showed improved resistance to hydrogen embrittlement when either of these elements was added to 4340 steel (19).

A. Powder Production and Characterization

1. Hydrogen Gas Atomization

The first approach involves hydrogen gas atomization of 4340 steel prealloyed with cerium by adding a 75% cerium - 25% nickel alloy to the melt. The hydrogen gas atomization process is a proven method of producing special alloy powders with low oxygen contents (22). The most commonly used method of making low alloy steel powders, water atomization, is not acceptable because the oxygen content of the powder produced by this process is in excess of 1000 ppm (23). This high oxygen level would probably result in the formation of massive rare earth oxide inclusions during subsequent powder processing. This first approach involves the preparation of at least two heats of hydrogen gas atomized 4340 steel powder, including one heat containing 0.2 percent cerium and one heat with no rare earth addition for control purposes. Additional heats of cerium-bearing 4340 steel powder are made, as necessary, to obtain the desired concentration (0.2%) of cerium in the powder. The 0.2 percent cerium level was chosen because maximum improvement in hydrogen embrittlement resistance occurred at this level in the previous study (19).

The hydrogen gas atomized 4340 steel powders are characterized by means of analysis of the chemical composition and metallographic examination of the microstructure. The main purpose of the chemical analyses is to determine the rare earth content of these powders and thus evaluate the degree of recovery of rare earth additions. The metallographic analyses include light microscopy, scanning electron microscopy, and electron microprobe analysis. The scanning electron microscopy is used to examine the characteristics of the loose powder particles, including their shape and overall size distribution. The light microscopy and electron microprobe analysis are used to examine the microstructure of the powder particles and to determine the location of the rare earth phases in the microstructure, as well as the degree of chemical segregation and the presence of impurities.

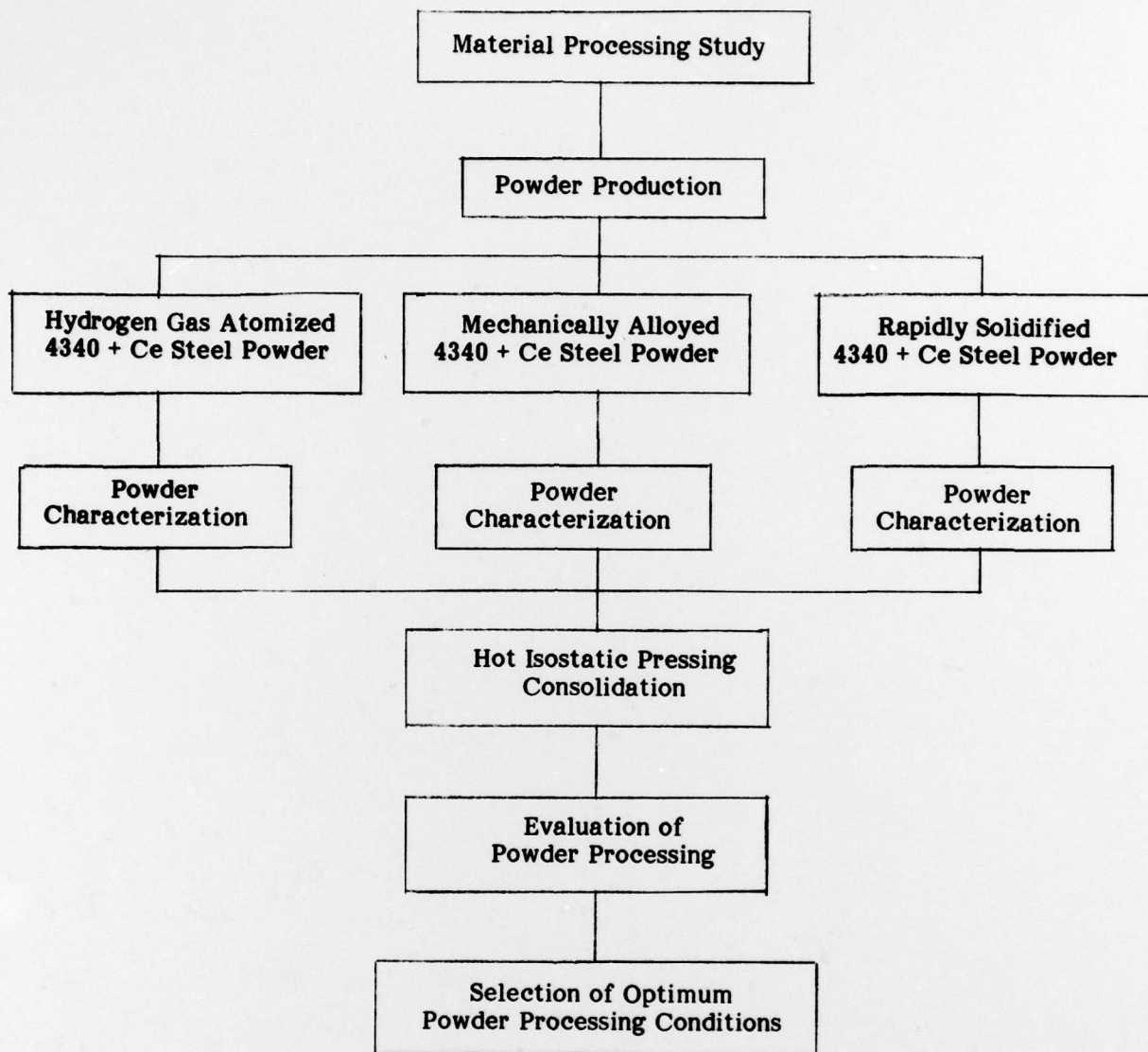


Figure 2. Flow Diagram of Current Program.

2. Mechanical Alloying

The second approach involves mechanical alloying of hydrogen gas atomized 4340 steel powder with either 75% cerium - 25% nickel alloy powder or lanthanum-nickel (LaNi_5) powder at a level of 0.2 weight percent. Mechanical alloying is a relatively new technique for forming alloys which cannot be produced by conventional melting methods (24-26). Mechanical alloying is accomplished by attriting different metal powders in a special high-intensity ball mill known as an attritor. Attriting results in a uniform distribution of alloying elements throughout the microstructure. In this second approach, six preliminary attriting trials are conducted in which the amount of rare earth compound powder added, the attriting ball size, the ball/powder ratio, and the attriting time are varied to produce optimum mechanical alloying, i.e., a uniform distribution of the rare earth additions in the steel microstructure. These preliminary attriting runs are conducted using small quantities of powder for efficiency and economy. The amount of rare earth compound powder added is varied because of variability in the degree of recovery of the rare earths in the attrited powders. Lanthanum was chosen as an additional rare earth element for the mechanical alloying study because of the availability of the LaNi_5 alloy which was specially developed for hydrogen absorption capability by the International Nickel Company. Lanthanum was also effective in improving the hydrogen embrittlement resistance of 4340 steel in the previous study (19). Using the optimum mechanical alloying conditions established in the preliminary attriting runs, three final attriting runs are made with sufficient powder for subsequent consolidation and mechanical property evaluation. In these three runs, the 4340 steel powder is attrited with (1) cerium-nickel powder, (2) LaNi_5 powder, and (3) no rare earth addition for control purposes.

The attrited powders from both the preliminary and final runs are characterized by chemical and metallographic analyses. The chemical analyses are used mainly to measure the rare earth content of these powders and hence determine the degree of recovery of the rare earth additions. The metallography involves light microscopy, scanning electron microscopy, and electron microprobe analysis. The scanning electron microscopy is utilized in examining the characteristics of the attrited powder particles, including their shape and overall size distribution. The light microscopy and electron microprobe analysis are used in examining the microstructure of the powder particles and in determining the degree of mechanical alloying as characterized by the break-up of particles.

3. Rapid Solidification Rate Atomization

The third method being explored consists of rapid solidification rate (RSR) atomization of 4340 steel prealloyed with cerium by adding a 75% cerium - 25% nickel alloy to the RSR melt. The RSR process is a newly developed technique for making high quality metal powders which enables more effective alloying and minimizes chemical segregation in the powder (27-29). This process allows the addition of greater quantities of alloying elements without the accompanying segregation effects which have proven detrimental to both subsequent processing and mechanical properties. Thus it is believed that the rapidly solidified steel powders can be alloyed with relatively large amounts of rare earth additions without the formation of massive grain boundary inclusions. This third approach involves the preparation of two heats of RSR atomized 4340 steel powder, one containing 0.2 percent cerium and the other with no rare earth addition for control purposes.

The rapidly solidified 4340 steel powders from both heats are characterized by chemical and metallographic analyses. The main purpose of the chemical analysis is to verify the cerium content of the rare earth modified heat and thus evaluate the degree of cerium recovery. Light microscopy, scanning electron microscopy, and electron microprobe analysis are included in the metallographic analyses. As with the hydrogen gas atomized powders, the scanning electron microscopy is employed to examine the characteristics of the loose powder particles, including their shape and overall size distribution. The light microscopy and electron microprobe analysis are used to examine the microstructure of the powder particles and to determine the location of the rare earth phases in the microstructure, as well as the degree of chemical segregation and the presence of impurities. In addition, these metallographic techniques are utilized to determine how the rapidly solidified 4340 steel powders differ from the hydrogen gas atomized powders.

B. Hot Isostatic Pressing Consolidation

Following powder characterization, the powders are consolidated by the hot isostatic pressing (HIP) process at a high temperature and a high pressure (30). This powder compaction process was selected because of the potential for obtaining a favorable compacted microstructure with this method. This includes a fully dense structure, no incipient melting, and a uniform distribution of rare earths. The most commonly used method of compacting low alloy steel powders, pressing and sintering, is not employed because steel powders produced by hydrogen gas atomization or RSR atomization are difficult to sinter. A number of HIP runs are performed in which the HIP temperature is varied to determine the optimum temperature for obtaining the most favorable microstructure. The as-HIP'ed compacts are then evaluated metallographically to determine whether a favorable compacted microstructure has been obtained.

C. Evaluation of Powder Processing

The HIP'ed powder metal compacts are heat treated and then evaluated by light metallography and mechanical property tests which include tensile and Charpy impact tests conducted at room temperature. Duplicate tensile and Charpy impact tests are performed on compacts of seven different types of 4340 steel powder: (1) hydrogen gas atomized powder with and without cerium; (2) attrited powder with cerium, lanthanum, and no rare earths; and (3) rapidly solidified powder with and without cerium. The specific processing conditions chosen for this testing depend on the results of the metallographic analyses of the HIP'ed compacts. The test specimens are heat treated to a yield strength level of approximately 200 ksi (1400 MPa) by austenitizing, quenching, and tempering at 450°F (505°K) for comparison with the previous results on rare earth modified 4340 steel (19).

D. Selection of Optimum Powder Processing Conditions

The final step in this material processing study is the selection of the optimum powder processing conditions. This selection is made on the basis of the metallographic and mechanical property evaluations of the HIP'ed powder metal compacts. These processing conditions include attriting parameters and HIP temperature.

III. PROGRAM STATUS

During the first year of the program, the research effort involved the development of material processing techniques for producing rare earth modified 4340 steel from metal powders. Work was conducted on all three approaches for making the metal powders, hydrogen gas atomization, mechanical alloying, and rapid solidification rate atomization, and the efforts in these three areas are continuing. The details of this work are described in the following sections.

A. Hydrogen Gas Atomization

1. Description of Process

The hydrogen gas atomization process, which is also known as the vacuum atomization or soluble gas process, was developed by Homogeneous Metals, Inc. (22). This method of making metal powders involves supersaturating the melt with highly pressurized hydrogen and imploding the gas-saturated molten metal through an orifice into a vacuum chamber, where the stream of pressurized liquid metal erupts into particles. The apparatus, which is illustrated in Figure 3, consists of a lower melting chamber which will maintain either pressure or vacuum and an upper expansion chamber which is maintained under a vacuum of <10 torr (31). The alloy is vacuum induction melted in the lower chamber and superheated before the chamber is pressurized with hydrogen gas. The ceramic transfer tube is dipped into the melt by raising the melting crucible. A valving mechanism is then actuated in the upper chamber and the gas-saturated molten metal is transferred to the expansion chamber through the ceramic tube. The metal leaves the tube orifice as a fine spray of molten droplets formed by the sudden release of the dissolved gas. The droplets are directed mainly upward by means of a nozzling arrangement. The cooled powder is drained from the expansion tank under vacuum into another tank which is then sealed off and back-filled with an inert gas. The size distribution of this powder is log normal and relatively broad, ranging from -20 mesh to less than 325 mesh. The average particle size can be controlled by varying the orifice size and the pressure differential, but the particles are generally irregular in shape rather than spherical.

The advantages of this method of atomization are that thorough mixing occurs during melting, porosity in the powder particles is low, and the oxygen content of the powder is generally less than 100 ppm. The major type of defect found in these powders is nonmetallic inclusions, which originate from crucible-melt reactions, transfer tube erosion, and slag particles. Another type of defect in these powders is cross contamination, which is due to other alloy particles remaining in the atomization unit or the powder classification screens from previous operations. Alloy powders based on nickel, cobalt, iron, copper, aluminum, and Misch metal have been made successfully by this process.

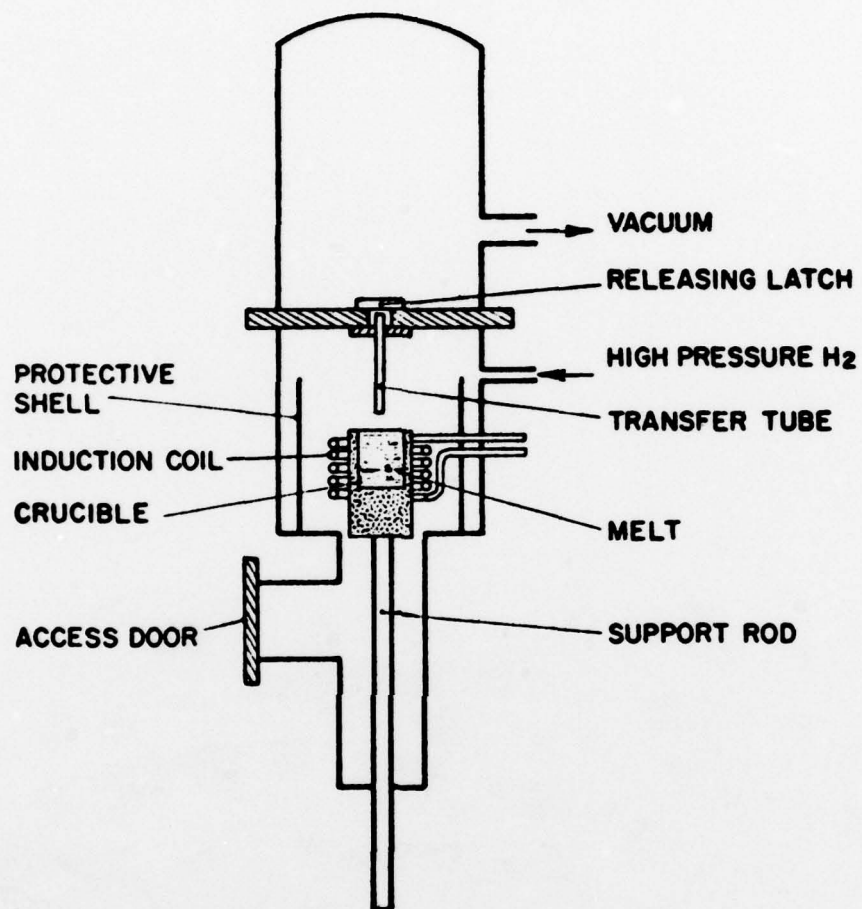


Figure 3. Hydrogen gas atomization unit for making metal powders (31).

2. Experimental Procedures

a. Powder Preparation

Four heats of 4340 steel powder were made by the hydrogen gas atomization process at Homogeneous Metals, Inc., under subcontract to TRW. One of these heats was a control heat containing no rare earth elements, while the other three heats contained cerium. The melt stock for these heats was obtained by making four 45-pound (20-kg.) ingots of 4340 steel without rare earths. These four ingots were vacuum-induction melted and aluminum deoxidized. These ingots were cast in the form of tapered rounds measuring 4 inches (0.10 m) in diameter at the bottom, 4-1/2 inches (0.11 m) in diameter at the top, and 9 inches (0.23 m) tall. The ingots were trimmed to 35-40 lbs (16-18 kg.) to remove the hot top and scale prior to melting. The chemical compositions of these ingots are presented in Table 1, along with the compositions of the resulting heats of powder.

The cerium was added to the melt in the form of 75% cerium - 25% nickel alloy chunks just seconds before atomization. Some difficulty was encountered with low cerium recovery in the resulting powders. The first run, powder heat X916, was made with no cerium addition, as this was the control heat. A cerium content of 0.2 weight percent was desired in the succeeding heats. For the second run, powder heat X917, enough cerium-nickel was added to the melt to obtain a cerium content of 0.2 weight percent in the resulting powder, assuming a cerium recovery of 80 percent. However, this heat contained only 0.004% cerium. In this run, the Ce-Ni alloy was added by suspending it on the end of a wire above the melt and then raising the melting crucible until the additive was submerged in the melt. Apparently, with this technique, the Ce-Ni additive floated and melted on the surface of the 4340 melt and thus did not mix well with the molten steel. For the third run, powder heat X971, the same percentage of cerium-nickel was added to the melt as in the second run, but the Ce-Ni alloy was added by suspending it on the end of a rigid rod above the melt to ensure that the additive would be submerged in the melt when the melting crucible was raised. This heat contained 0.043% cerium, indicating a cerium recovery of only about 20 percent. Therefore, for the fourth run, powder heat X989, five times more cerium-nickel was added to the melt, using the same technique as in the third run. The cerium content of this heat was 0.24%. The cause of the low cerium recovery (20 percent) in the third and fourth atomization runs was not established, but losses due to oxidation and segregation in coarse particles and flakes are plausible explanations. By comparison, the cerium recovery in the vacuum-induction melted 4340 steel heats made in the previous studies was about 80 percent (19-21), which suggests that most of the cerium loss in the powders was associated with the process of atomization.

Losses also occurred in two of the other alloying elements, manganese and nickel. As shown in Table 1, the manganese content of the powder was lower than that of the corresponding ingot for all four runs. This was attributed to the low vapor pressure of manganese. Conversion of the ingot to powder resulted in a substantial loss of nickel (from 1.80% to 0.55%, Table 1) in the first run only, and this reduction could not be explained. Aluminum pickup occurred in three of the four runs (Table 1), and this was attributed to reaction of the melt with the alumina melting crucible and the alumina transfer tube.

Table 1

Chemical Compositions of 4340 Steel Ingots and Powders, Weight Percent

Element	AISI 4340 Specification	Run #1		Run #2		Run #3		Run #4	
		Y451	X916	Y452	X917	Y453	X971	Y626	X989
(Heat No.)	-								
C	0.38-0.43	0.42	0.42	0.40	0.40	0.40	0.40	0.40	0.33
Mn	0.60-0.80	0.66	0.35	0.66	0.48	0.64	0.55	0.75	0.68
P	0.040 max.	< 0.008	0.011	< 0.008	0.012	< 0.008	0.011	< 0.008	0.006
S	0.040 max.	0.005	0.005	0.005	0.012	0.005	0.002	0.005	0.002
Si	0.20-0.35	0.30	0.24	0.30	0.32	0.30	0.33	0.32	0.45
Ni	1.65-2.00	1.80	0.55	1.80	2.06	1.80	1.95	1.85	2.10
Cr	2.70-0.90	0.76	0.78	0.76	0.67	0.78	0.86	0.85	0.86
Mo	0.20-0.30	0.26	0.35	0.27	0.31	0.27	0.24	0.24	0.31
Al	-	0.043	0.23	0.043	0.17	0.044	0.028	0.044	0.085
O	-	-	0.0142	-	0.021	-	0.028	-	0.090
N	-	-	0.002	-	0.002	-	0.0005	-	0.0012
Ce	-	-	-	-	0.004	-	0.043	-	0.24

The powders were screened to -80 mesh size for subsequent processing. The yields of -80 mesh powder were as follows:

<u>Heat Number</u>	<u>Weight of -80 Mesh Powder</u> <u>Lb. (Kg.)</u>
X916	9.8 (4.4)
X917	9.5 (4.3)
X971	23.5 (10.7)
X989	27.5 (12.5)

The yields of the last two heats were higher than the first two because argon was added to the atomizing gas (50% H₂ + 50% Ar) to increase the yield of -80 mesh powder. The losses consisted of coarse particles (+80 mesh), flake, and the melting skull.

b. Powder Consolidation

Powders from heats X916 and X971 were compacted by HIP consolidation at Industrial Materials Technology, Inc., under subcontract to TRW. These two heats were chosen for HIP consolidation because of the desire to compact one heat containing cerium and one heat without cerium. Heat X917 was not selected because the cerium content was too low (0.004%) and heat X989 (0.24% Ce) had not yet been atomized when the HIP operations were performed. The most commonly used method of compacting low alloy steel powders, pressing and sintering, was not employed because steel powders produced by hydrogen gas atomization are difficult to sinter (32). In the HIP process, the powder is enclosed in a can and outgassed, the can is sealed under vacuum, and then the can is placed in an autoclave at a high temperature and a high pressure for a specified length of time (30). After removal from the autoclave, the can material is removed from the compacted powder by machining or chemical dissolution. The shape of the can determines the shape of the powder compact. The choice of can material, usually carbon steel or stainless steel, depends on the powder alloy and the particular application. The selection of HIP temperature, pressure, and time depends on the composition of the powder alloy and the characteristics of the powder.

In the present study, round cylindrical carbon steel HIP cans were employed to produce round bar powder compacts. The HIP consolidation was conducted at a pressure of 15,000 psi (103 MPa) for 2 hours and at temperatures of 1800 and 2000°F (1260 and 1370°K). A total of twelve bars were made by this process, six of heat X916 (0% Ce) powder and six of heat X971 (0.043% Ce) powder. Three of the six bars of each heat were HIPed at 1800°F (1260°K) and the other three at 2000°F (1370°K). These bars measured 9/16 inch (0.014 m) in diameter by 9 inches (0.23 m) long after the can material was removed by machining on a lathe.

c. Powder Evaluation

The powder compacts were evaluated by metallographic analysis and mechanical property tests on heat treated specimens. The metallographic analyses were performed on 1/4-inch (0.0064 m) thick slices cut from the bars. The mechanical properties of the bars HIPed at 2000°F (1370°K) were evaluated by performing duplicate tensile and Charpy

impact tests at room temperature on specimens machined from these bars. One tensile specimen and one Charpy impact specimen were taken from each of four bars, with two of these bars being made of heat X916 (0% Ce) powder and two of heat X971 (0.043% Ce) powder. The mechanical properties of the bars HIP'ed at 1800°F (1260°K) were not evaluated because the metallographic examination of this material revealed that it had been incompletely compacted. The dimensions of the tensile and Charpy impact specimens are shown in Figure 4. These test specimens were rough machined from the bars, heat treated, and then finish ground to their final dimensions. The heat treatment consisted of the following:

1. Normalize at 1700°F (1200°K) for 15 minutes in argon atmosphere and air cool.
2. Austenitize at 1550°F (1120°K) for 30 minutes in argon atmosphere and oil quench.
3. Temper at 450°F (505°K) for 1 hour plus 1 hour in air, and air cool.

The 450°F (505°K) tempering temperature was chosen for comparison with the previous results on rare earth modified 4340 steel (19).

3. Results and Discussion

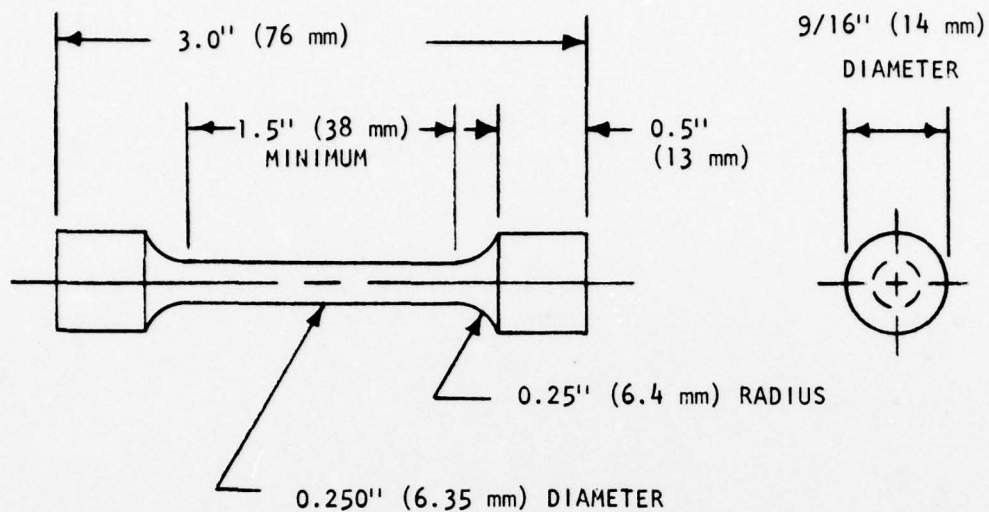
a. Powder Characterization

Photographs taken in the scanning electron microscope of samples of the loose powders from heats X916 and X917 are shown in Figure 5. The irregular shape of the powder particles and the smaller satellite particles attached to the larger particles are typical of powders made by the hydrogen gas atomization process (22,31). No significant differences in the size or shape of the particles were observed between the powder containing cerium (heat X917) and the powder without cerium (heat X916). Photomicrographs taken in the light microscope of these powders are shown in Figure 6 and indicate that they are clean and relatively free of nonmetallic inclusions. Again, no differences were observed between the two heats of powder.

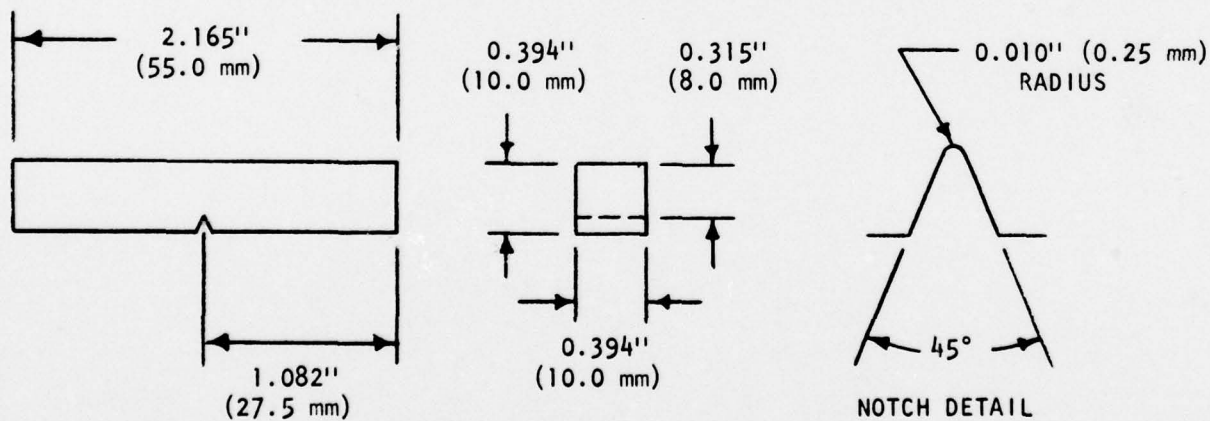
The oxygen contents of the four heats of hydrogen gas atomized 4340 steel powder were higher than expected, as indicated in Table 1. The oxygen content of powders made by this process is usually less than 100 ppm (31). However, the oxygen levels of the four heats were all higher than 100 ppm and increased with increasing cerium content, ranging from 142 ppm for the heat with no cerium (X916) to 900 ppm for the heat with 0.24% cerium (X989). The higher oxygen contents of the cerium-bearing heats were attributed to the combination of the cerium, which is a strong oxygen getter, with the residual oxygen in either the hydrogen atmosphere during melting or the vacuum atmosphere during atomization.

b. HIP Consolidation

The HIP consolidation at 1800°F (1260°K) resulted in incomplete compaction of the powder, as shown in Figure 7, indicating that this temperature was too low for complete consolidation. This condition would be extremely detrimental to

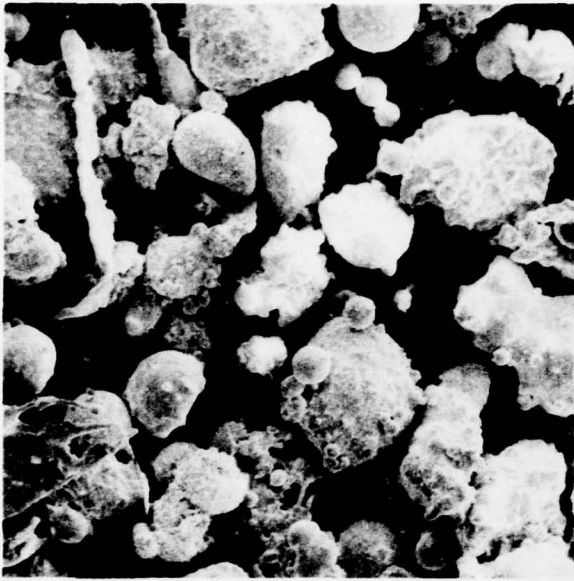


(a) Tensile test specimen.

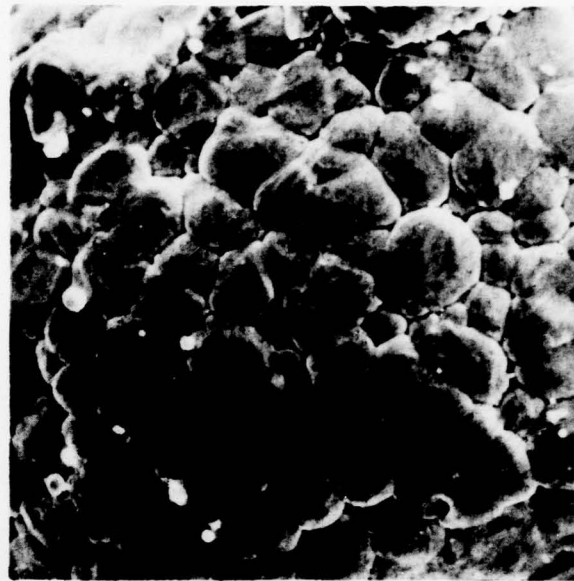


(b) Charpy impact test specimen.

Figure 4. Tensile and Charpy impact test specimens used to evaluate mechanical properties of powder metallurgy 4340 steels.

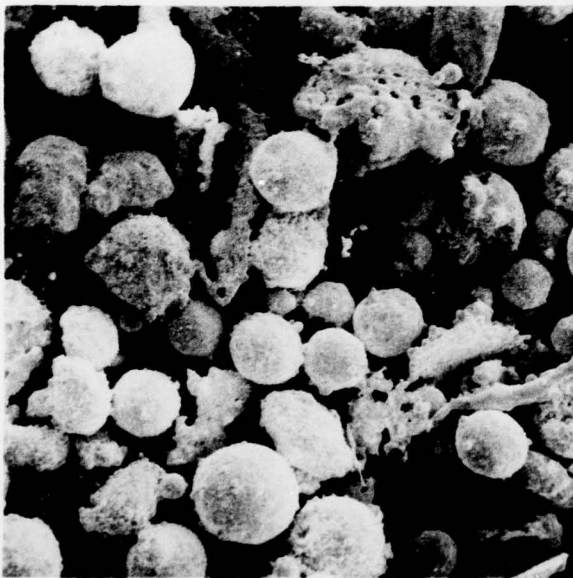


Magnification, 100X

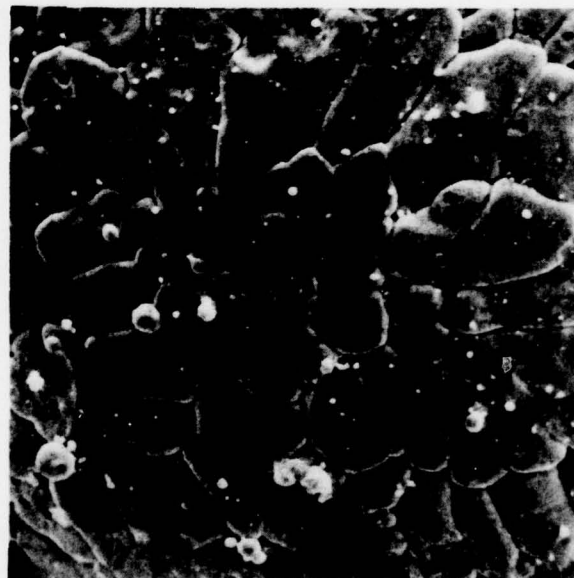


Magnification, 1000X

Heat X916 (0% Ce)



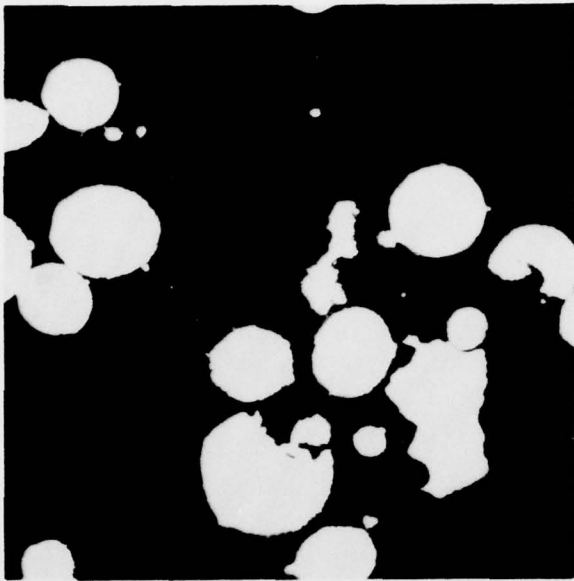
Magnification, 100X



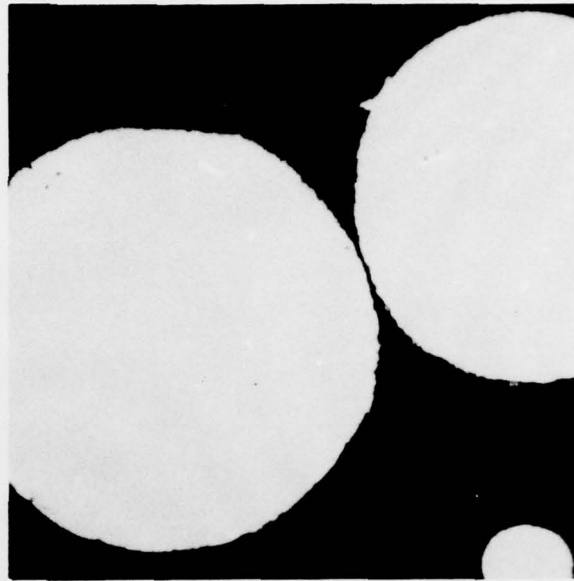
Magnification, 1000X

Heat X917 (0.004% Ce)

Figure 5. SEM photographs of hydrogen gas atomized 4340 steel powders.

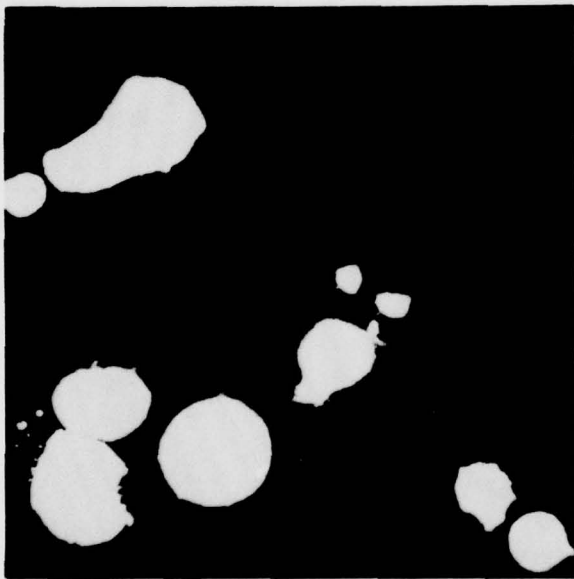


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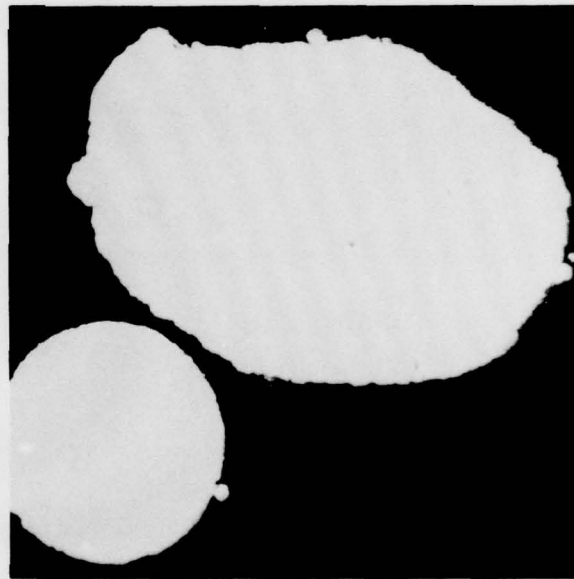


Magnification, 500X

Heat X916 (0% Ce)



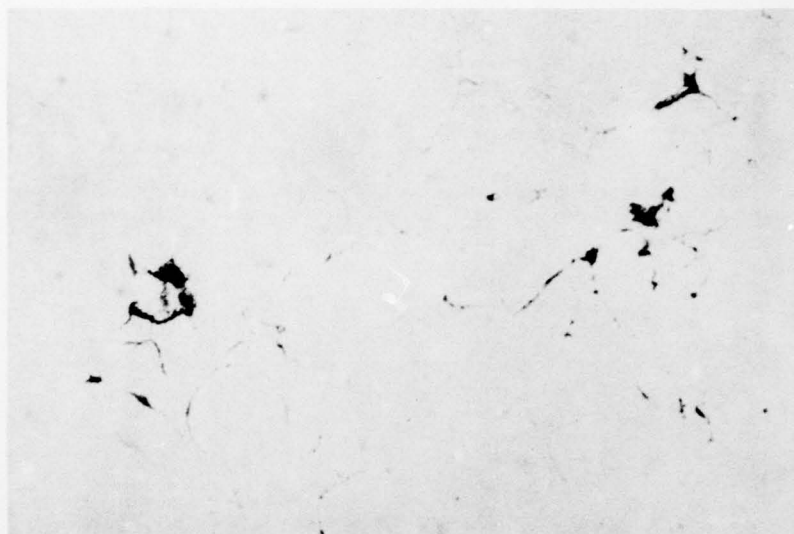
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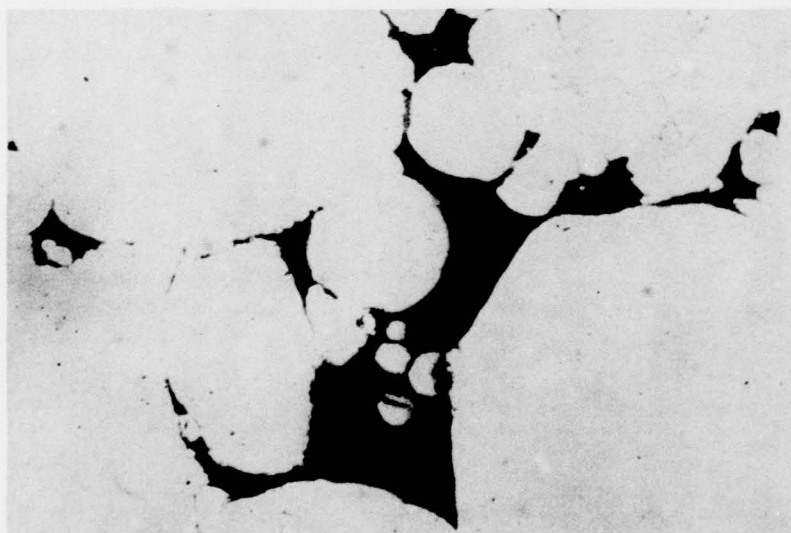
Magnification, 500X

Heat X917 (0.004% Ce)

Figure 6. Light photomicrographs of hydrogen gas atomized 4340 steel powders, unetched.



Magnification, 500X



Magnification, 500X

Figure 7. Light photomicrographs of hydrogen gas atomized 4340 steel powder from heat X916 HIP'ed at 1800°F (1260°K), unetched, showing incomplete compaction.

mechanical properties because of the effect of the large voids between incompletely bonded particles. Because of this condition, no further evaluation was performed on the material that was HIP'ed at 1800°F (1260°K).

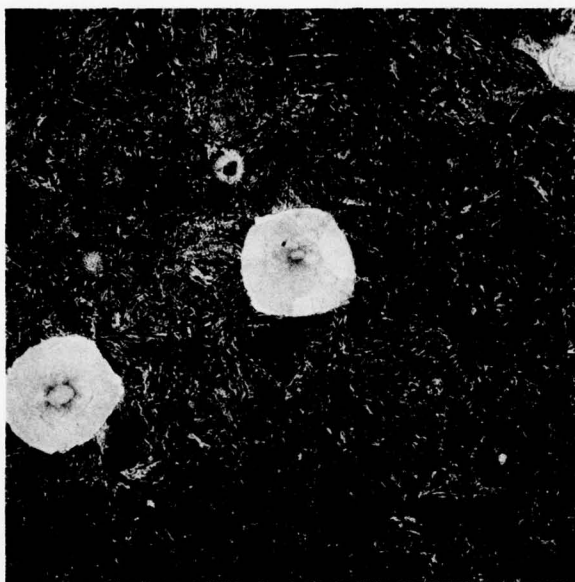
There was no evidence of incomplete compaction in the bars HIP'ed at 2000°F (1370°K). Photomicrographs of these bars are shown in Figure 8. Another type of defect is evident in these photomicrographs, and this appears to be cross contamination particles. These particles did not respond to the etching as the steel did, indicating that they may be from a different alloy. The presence of these suspected foreign particles in the material indicates that the powder production equipment may not have been entirely free of particles remaining from previous operations with other alloys. Such contaminant particles can be detrimental to mechanical properties, particularly those properties which involve a crack initiation and growth process, such as fatigue strength and hydrogen embrittlement resistance (33).

c. Evaluation of HIP'ed Compacts

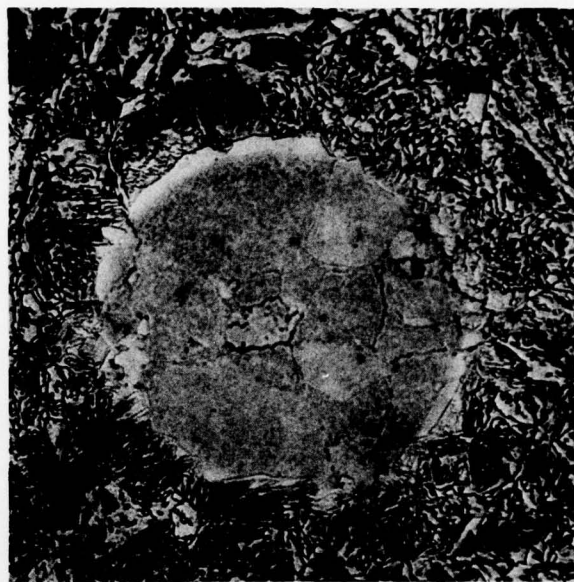
Photomicrographs of the 2000°F (1370°K) HIP'ed bars after heat treatment are shown in Figure 9. Except for the suspected contaminant particles, the microstructure consisted of tempered martensite, which is typical of 4340 steel in the quenched and tempered condition.

The mechanical properties of the bars HIP'ed at 2000°F (1370°K) are presented in Table 2, along with the mechanical properties of wrought 4340 steel plates with and without cerium, heat treated the same as the HIP'ed bars, evaluated previously (19). The mechanical properties of the HIP'ed bars were expected to approach those of the wrought plates. However, except for the ultimate tensile strength of the specimen from bar 9G254D, the mechanical properties of the HIP'ed bars were much lower than those of the wrought plates. The tensile specimens failed in such a brittle manner that it was not possible to obtain yield strength values for any of the four specimens or to obtain any measurable elongation or reduction of area for three of the specimens. The fracture surfaces of these three tensile specimens were flat and granular in appearance, while the fracture surface of the specimen from bar 9G254D (i.e., the one with the high tensile strength) had a fibrous appearance and a small shear lip around its perimeter, similar to the appearance of the fracture surfaces of the tensile specimens from the wrought plates. The fracture surfaces of the Charpy impact specimens were similar to those of the tensile specimens taken from the same bars, i.e., three were flat and granular in appearance, while the fracture surface of the specimen from bar 9G254D had a fibrous appearance and small shear lips along its sides.

Photographs taken in the scanning electron microscope of the fracture surface of the tensile specimen from bar 9G253D, one of the three more brittle specimens, are shown in Figure 10. These photographs indicate that the fracture path was primarily intergranular. Photomicrographs taken in the light microscope of a longitudinal section through the fracture surface of this specimen, shown in Figure 11, also indicate that the fracture path was mainly intergranular. The networks of secondary cracks near the fracture surface, Figure 11, suggest that the intergranular fracture path was along prior particle boundaries rather than prior austenite grain boundaries, since these networks appear to outline prior particles. The cracking along the prior particle boundaries is indicative of a

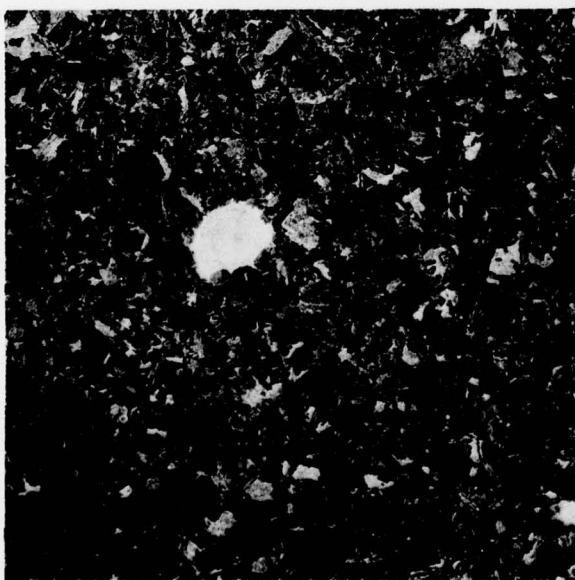


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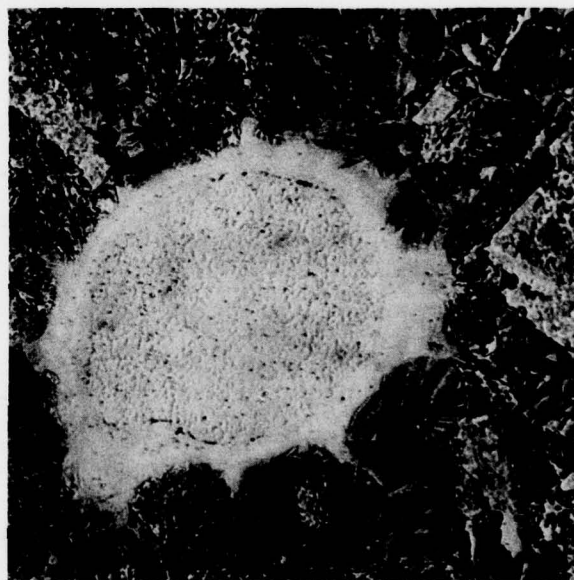


Magnification, 500X

Heat X916 (0% Ce)



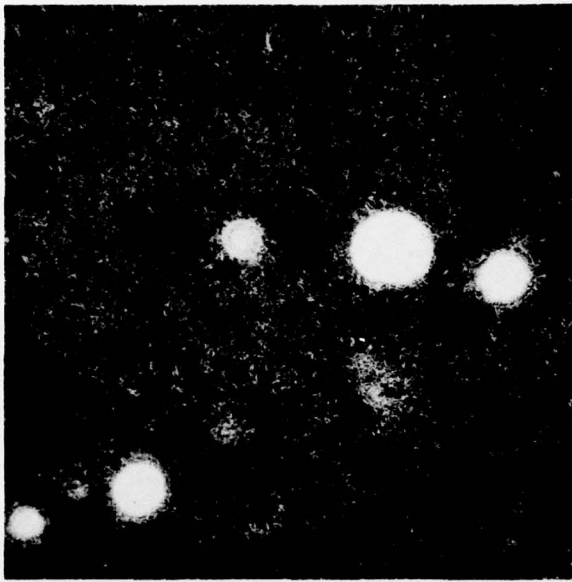
Magnification, 100X



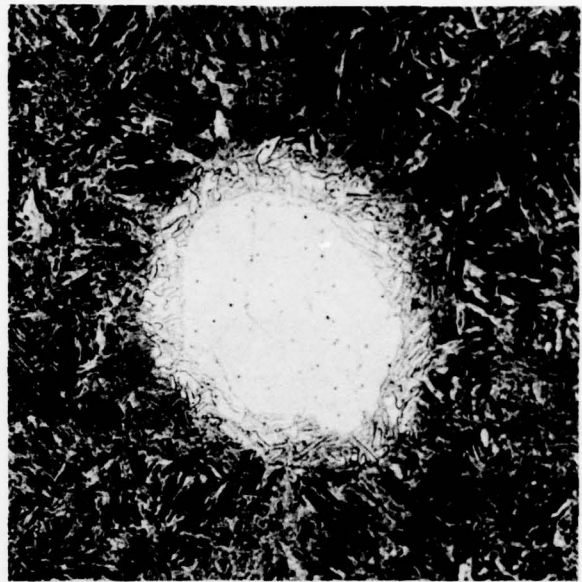
Magnification, 500X

Heat X971 (0.043% Ce)

Figure 8. Light photomicrographs of hydrogen gas atomized 4340 steel powders HIP'ed at 2000° F (1370° K), etched with nital.

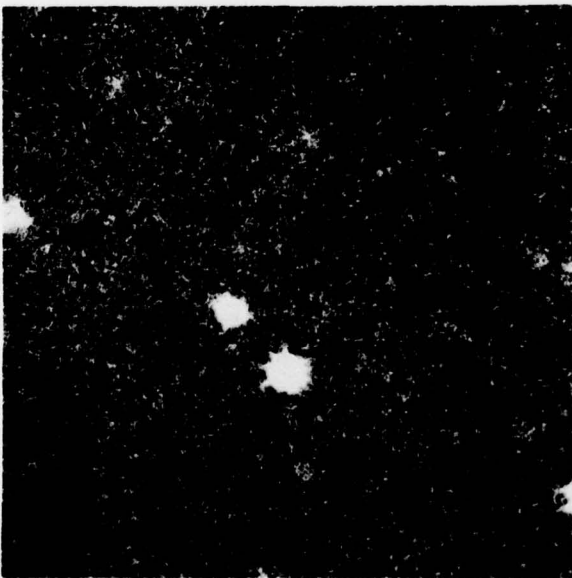


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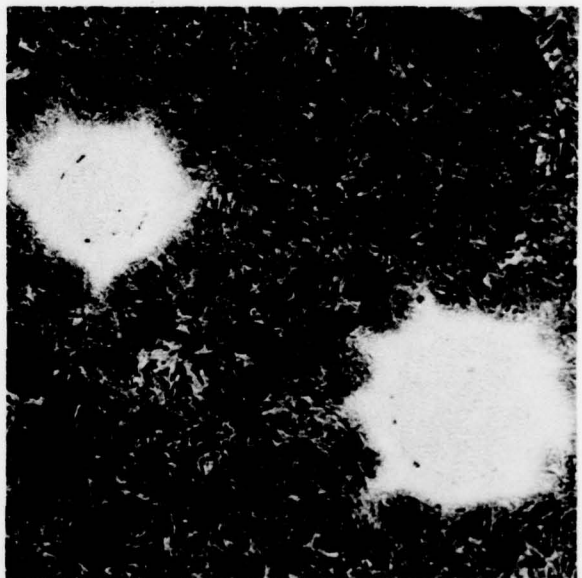


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Heat X916 (0% Ce)



Magnification, 100X



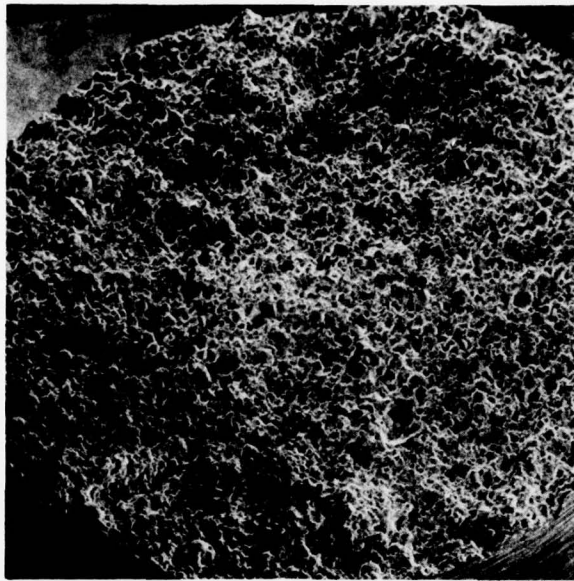
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Heat X971 (0.043% Ce)

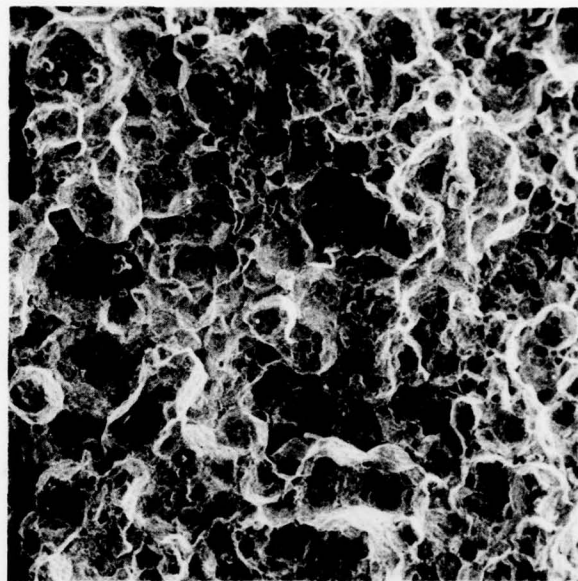
Figure 9. Light photomicrographs of hydrogen gas atomized 4340 steel powders HIP'ed at 2000° F (1370° K) and heat treated, etched with nital.

Table 2
Mechanical Properties of 4340 Steel HIP'ed Bars and Wrought Plates

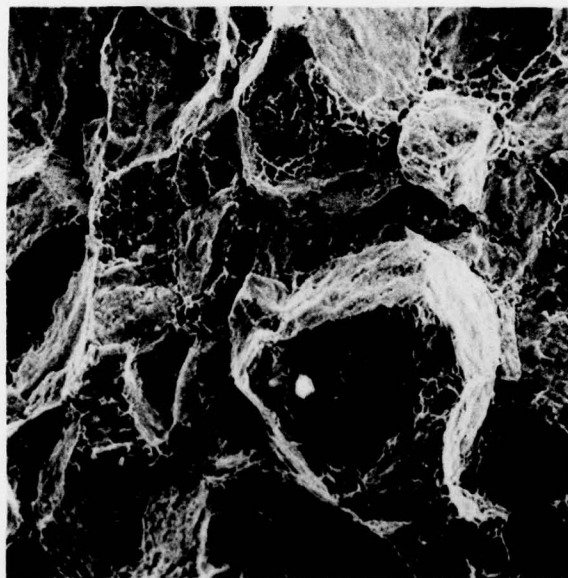
Heat/Bar No.	Cerium Content %	Yield Strength at 0.2% Offset		Ultimate Tensile Strength		Elongation %	Reduction of Area %	Charpy Impact Energy	
		ksi	MPa	ksi	MPa			ft-lb	J
Bars HIP'ed at 2000°F (1370°K)									
X916/9G253D	0	-	-	184	1270	0	0	1.5	2.0
X916/9G253E	0	-	-	154	1060	0	0	1.0	1.4
X971/9G254D	0.043	-	-	268	1850	5.5	12.3	6.5	8.8
X971/9G254E	0.043	-	-	106	731	0	0	1.5	2.0
Wrought Plates									
X409	0	206	1420	254	1750	13.3	50.4	23.5	31.9
X421	0.17	200	1380	248	1710	10.3	34.7	10.5	14.2



Magnification, 16X

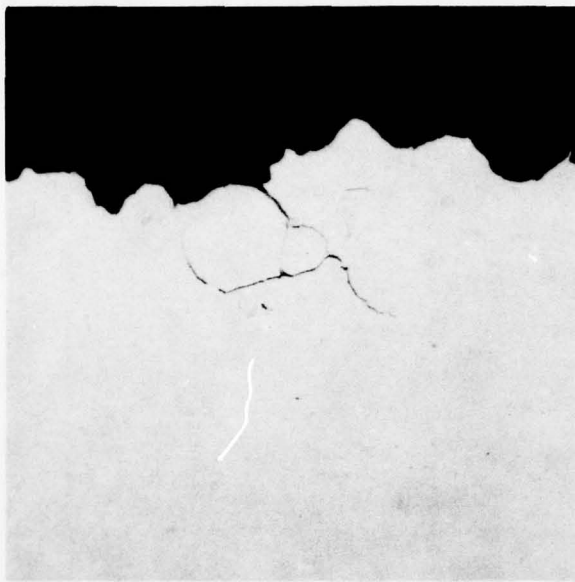


Magnification, 100X

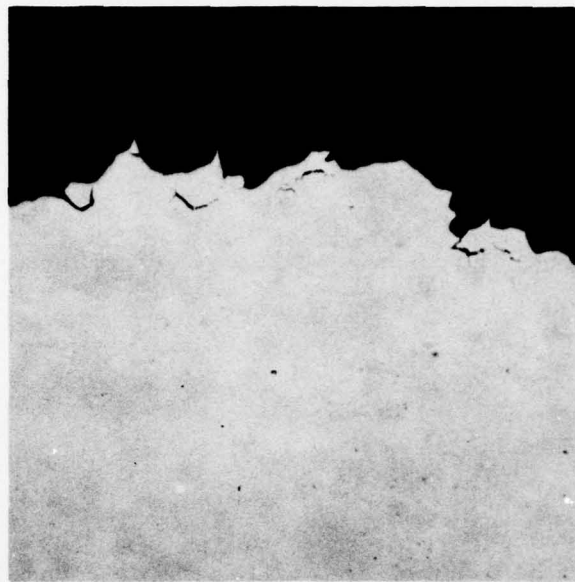


Magnification, 500X

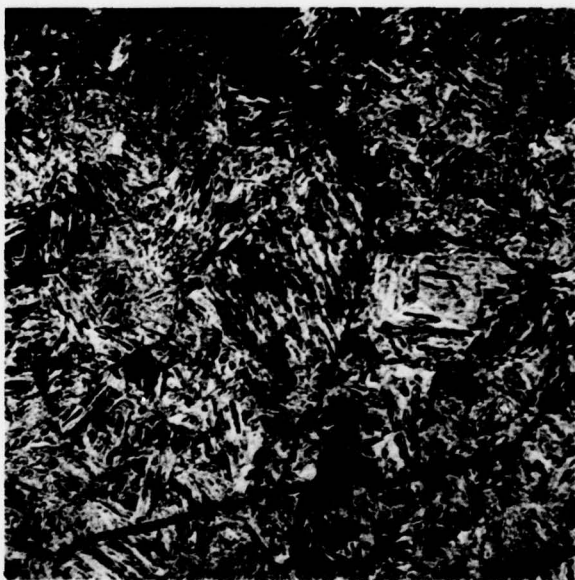
Figure 10. SEM photographs of fracture surface of tensile specimen from bar 9G253D, which was made of 4340 steel powder without cerium from heat X916 and HIP'ed at 2000° F (1370° K).



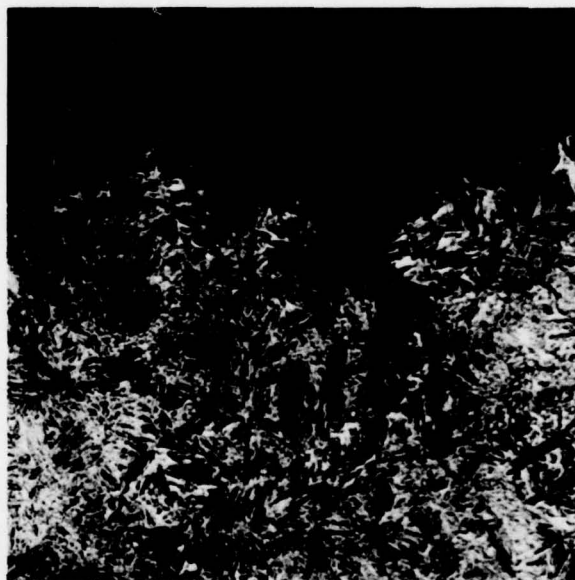
Area A, unetched
Magnification, 100X



Area B, unetched
Magnification, 100X



Area A, nital etched
Magnification, 500X



Area B, nital etched
Magnification, 500X

Figure 11. Light photomicrographs of longitudinal section through fracture surface of tensile specimen from bar 9G253D, which was made of 4340 steel powder without cerium from heat X916 and HIP'ed at 2000° F (1370° K).

brittle condition in these boundaries. This condition probably developed during the HIP operation rather than during the atomization of the powder since one of the bars (9G254D) did not exhibit this brittle intergranular condition while the other bar (9G254E) from the same heat of powder (X971) did. This condition was undoubtedly responsible for the poor mechanical properties of three of the four HIP'ed bars. The fracture path did not appear to be associated with the cross contaminant particles observed in the microstructure after HIP (Figure 8) and after heat treatment (Figure 9). The nature of the prior particle boundaries is currently being investigated to ascertain the cause of the cracking along these interfaces. Although bar 9G254D did not exhibit this brittle intergranular condition and the ultimate tensile strength of this bar was higher than that of the wrought plates, the ductility and impact resistance of this bar were still much lower than those of the wrought plates (Table 2). The cause of this degradation is also under investigation.

4. Summary and Conclusions

The hydrogen gas atomization process was used to make four heats of 4340 steel powder, one heat with no rare earth additions for control purposes and three heats containing cerium. The cerium was added as 75% Ce - 25% Ni alloy chunks to the molten steel prior to atomization. The degree of cerium recovery in the powder (20 percent) was much lower than had been anticipated (80 percent), so that the desired cerium content of 0.2 percent was obtained in only one heat. The powders were screened to -80 mesh size for subsequent processing. Scanning electron microscopy of the loose powders showed that the particles were irregular in shape, which is typical of powders made by this process. Light microscopy of these powders indicated that they were clean and relatively free of nonmetallic inclusions. No significant differences were observed in either the scanning electron microscope or the light microscope between powder with no cerium and powder containing 0.004% cerium. The oxygen contents of the four heats of powder were all higher than had been anticipated (<100 ppm) and increased with increasing cerium content, ranging from 142 ppm for the heat without cerium to 900 ppm for the heat with 0.24% cerium. This was attributed to the strong oxygen getter behavior of cerium, which apparently combined with the residual oxygen in the controlled atmospheres during melting and atomization.

Powders from two of the heats, one containing 0.043% cerium and the other with no cerium, were compacted by hot isostatic pressing (HIP) consolidation at a pressure of 15,000 psi (103 MPa) for 2 hours and at temperatures of 1800 and 2000°F (1260 and 1370°K) to produce round bars. The HIP consolidation at 1800°F (1260°K) resulted in incomplete compaction of the powder, indicating that this temperature was too low for complete consolidation, so no further evaluation was conducted on this material. The bars HIP'ed at 2000°F (1370°K) appeared to be completely compacted but contained what appeared to be cross contamination particles. Samples of these bars were heat treated by normalizing, austenitizing, quenching, and tempering at 450°F (505°K), the same heat treatment used previously for wrought plates of rare earth modified 4340 steel, resulting in a microstructure consisting of tempered martensite except for the suspected contaminant particles. The mechanical properties of these bars after heat treatment were generally much lower than those of the wrought plates, and the failures in three of four bars evaluated were brittle and intergranular. These results were attributed to a brittle condition in the prior particle boundaries. This condition probably developed during the HIP operation rather than during atomization of the powder, since one of the bars evaluated did not exhibit this brittle intergranular condition. The fracture path did not appear to be associated with the cross contaminant particles. The investigation of the cause of failure along the prior particle boundaries is continuing.

B. Mechanical Alloying

1. Description of Process

The mechanical alloying process was developed by the International Nickel Company as a means of combining the advantages of gamma-prime precipitation hardening for intermediate temperature strength and oxide dispersion strengthening for high temperature strength in a nickel-base superalloy (24-26). However, the process is also applicable to a large number of alloy systems which, because of liquid or solid phase segregation, high melting temperature, or very high reactivity, are not amenable to production by conventional techniques. In this process, a blend of powders is subjected to highly energetic compressive impact forces such as those occurring in a high energy stirred ball mill, shaker mill or vibratory ball mill. The starting charge usually consists of a blend of elemental, master alloy, and compound powders of very different characteristics and initial particle sizes. Interdispersion of the ingredients occurs by repeated cold welding and fracture of the powder particles. During each collision of the grinding balls, many powder particles are trapped and plastically deformed. Along the line of centers between the colliding balls, sufficient plastic deformation can occur to rupture the adsorbed surface contaminant film on the particles, exposing atomically clean metal surface. Since such surfaces oxidize readily, the milling operation is conducted in an atmosphere of nitrogen or an inert gas. Where metal particles overlap, cold welds are formed at the clean surfaces, building up composite metal particles, while other powder particles are fractured. Later in the process, most of the particles consist of composites and the structure is refined. While some composite particles are welded together into larger composites, other composite particles, which are less able to withstand the plastic deformation required for cold welding, are fractured. The cold welding and fracturing of the particles reach a steady-state balance, resulting in a relatively coarse and stable overall particle size. The internal structure of the metal particles is continually refined by the repeated plastic deformation. The mechanical alloying process is unique in that it is an entirely solid state process, allowing dispersion of insoluble phases such as refractory oxides and addition of reactive alloying elements such as aluminum and titanium.

2. Experimental Procedures

The mechanical alloying experiments were conducted by attriting the metal powders in a Szegvari Pilot Laboratory Model No. 1-5 Attritor. A photograph of this machine is shown in Figure 12. An attritor is a high energy stirred ball mill in which the charge of balls and powder is held in a stationary, vertical, water cooled tank and agitated by impellers radiating from a rotating central shaft, as illustrated in Figure 12. Six preliminary attriting runs were conducted using the conditions given in Table 3, in order to determine the effects of the amount of rare earth compound powder added, the attriting ball size, the ball/powder ratio, and the attriting time on mechanical alloying of the rare earth elements with the 4340 steel powder. The objective here was to obtain a uniform distribution of the rare earth additions in the steel microstructure. The optimum mechanical alloying conditions established in these preliminary attriting runs are then used in the final attriting runs which are scaled up with sufficient powder for subsequent consolidation and mechanical property evaluation.

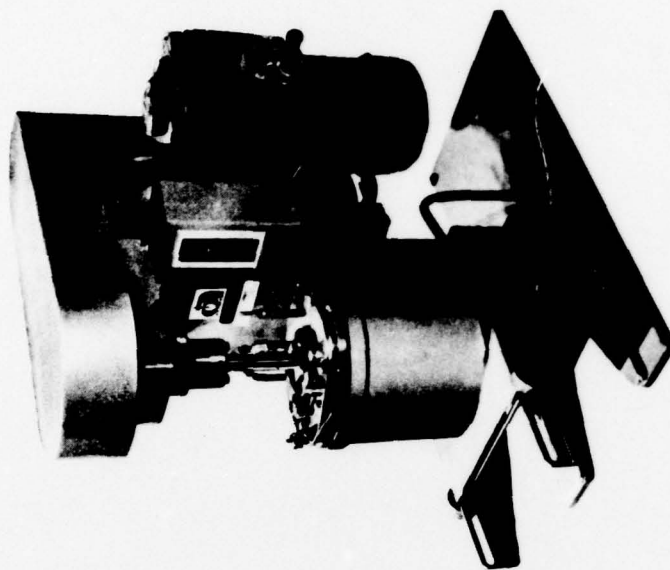
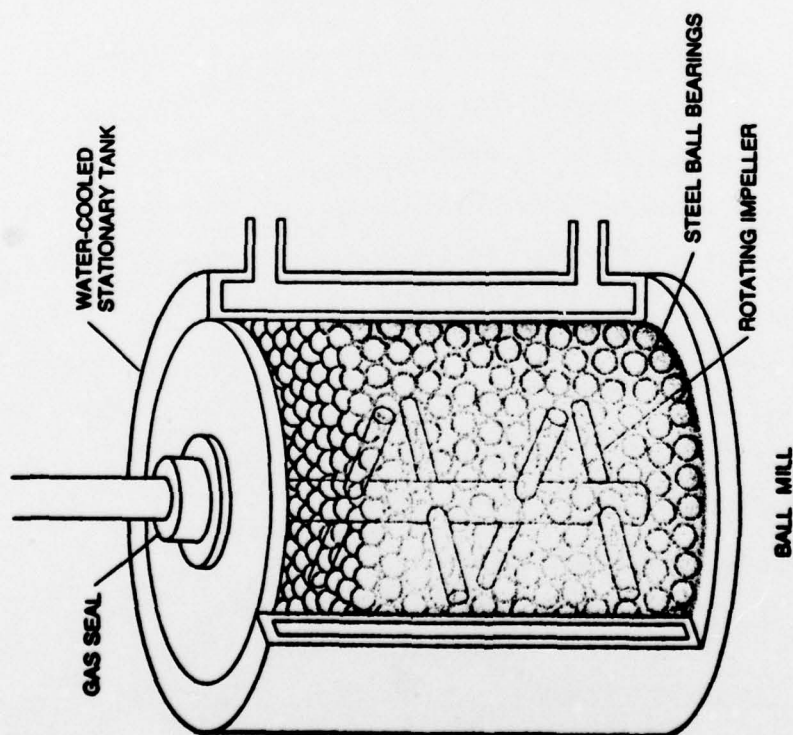


Figure 12. Photograph of Szegvari Pilot Laboratory Model No. 1-S Attritor (left) and illustration of attriting process (right).

Table 3

Attriting of 4340 Steel Powder

<u>Run Number</u>	<u>Rare Earth Addition</u>	<u>Grinding Ball Diameter Inches (m.)</u>	<u>Attriting Time Hours</u>	<u>Rare Earth Content of Powder</u>	<u>Oxygen Content of Powder ppm</u>
1	-	1/8 (0.0032)	25	-	-
2	0.3% Ce	1/8 (0.0032)	25	0.10% Ce	2100
3	0.3% Ce	1/8 (0.0032)	50	0.18% Ce	2500
4	0.3% La	1/8 (0.0032)	50	0.13% La	2000
5	0.3% La	3/16 (0.0048)	50	0.090% La	1700
6	0.3% Ce	3/16 (0.0048)	25	0.10% Ce	880

Hydrogen gas atomized 4340 steel powder from heat X916, containing no rare earths, was used as the master alloy powder in all six preliminary runs. This powder was used in the as-atomized condition for the first five runs, while for the sixth run the steel powder was first annealed at 1200°F (920°K) for 2 hours in a vacuum. The mass of the steel powder charge was 0.40 lbs. (0.18 kg.) for each of the first five runs and 2.0 lbs. (0.91 kg.) for the sixth run. Cerium and lanthanum were added to the starting charge for runs 2 through 6 in the form of 75% cerium - 25% nickel alloy granules and LaNi₅ alloy granules, respectively. Photographs of these additives taken in the scanning electron microscope are shown in Figure 13. Sufficient 75% Ce - 25% Ni or LaNi₅ was added to the charge to obtain a rare earth content of 0.3 weight percent in the starting charge for these five runs. The grinding balls used in all six runs were carbon steel balls, either 1/8 inch (0.0032 m.) or 3/16 inch (0.0048 m.) in diameter. The mass of the grinding balls used in each of the six runs was 10 lbs. (4.5 kg.), resulting in a ball/powder ratio of 25:1 for the first five runs and 5:1 for the sixth run. All six runs were conducted in an atmosphere of argon gas to minimize oxidation of the metal powder particles.

3. Results and Discussion

The results of the six preliminary attriting runs are presented in Table 3. The rare earth contents of the attrited powders from runs 2 through 6 were only 30 to 60 percent of the rare earth contents of the starting charges, indicating that much of the rare earth additions were lost during attriting. These losses are believed to have occurred at the bottom of the attritor tank where the impellers are less effective. These losses were probably much larger than would be expected because the charge sizes in these preliminary runs were much smaller than the capacity of the attritor tank, which was 0.50 gallon (1.9 liters). Increasing the mass of the starting charge of powder from 0.40 lbs. (0.18 kg.) in the first five runs to 2.0 lbs (0.91 kg.) in the sixth run did not reduce the rare earth loss in the attrited powder, as this larger charge was still much smaller than the attritor tank capacity.

The attriting operation increased the oxygen content of the steel powder from 142 ppm (Table 1, heat X916) in the starting charge to the order of 2000 ppm in the attrited powders, except for run 6 (Table 3). This increase in oxygen content was probably due to residual oxygen which was present in the argon atmosphere and was picked up by the steel powder particles and the rare earth additive particles.

Photographs taken in the light microscope of attrited powder particles from the six preliminary runs are shown in Figures 14 through 16. The microstructures of the particles from the first five runs were only slightly deformed, indicating that the attriting process in these runs was not effective. Because of this, no effects of attriting ball size, ball/powder ratio, or attriting time could be observed. The lighter etching surface layer on some of these particles was probably the result of softer particles being cold welded to harder particles. This surface layer was analyzed in several different particles in the electron microprobe and found to be of the same nominal chemical composition as the interior of the particles. No significant rare earth content was found in either the surface layer or the interior of the particles, indicating that no significant mechanical alloying had occurred. The ineffectiveness of the attriting process in the first five runs was attributed to the hardness of the steel powder particles as a result of rapid cooling during atomization. Therefore, the steel powder for the sixth run was annealed prior to attriting. The microstructure of particles from this run, shown in Figure 16, was heavily deformed,

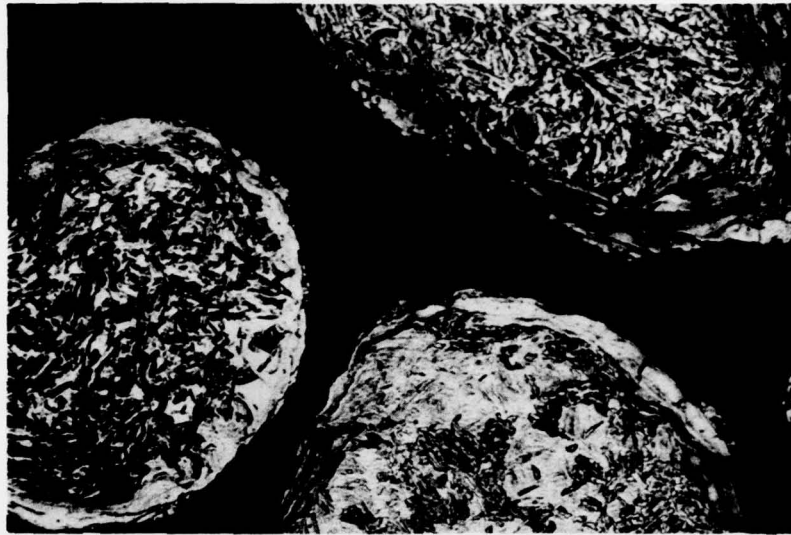


Cerium-Nickel (75%Ce-25%Ni)
Magnification, 20X

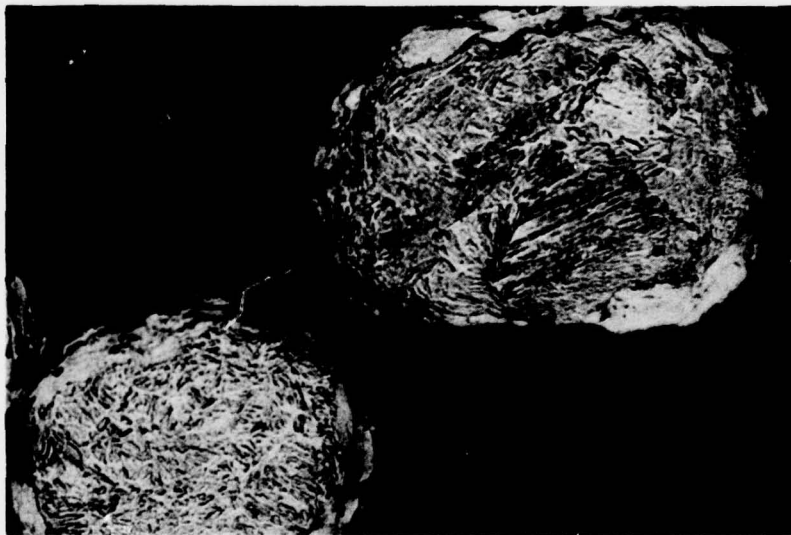


Lanthanum-Nickel (LaNi₅)
Magnification, 50X

Figure 13. SEM photographs of rare earth compound additives used for mechanical alloying with 4340 steel powder.

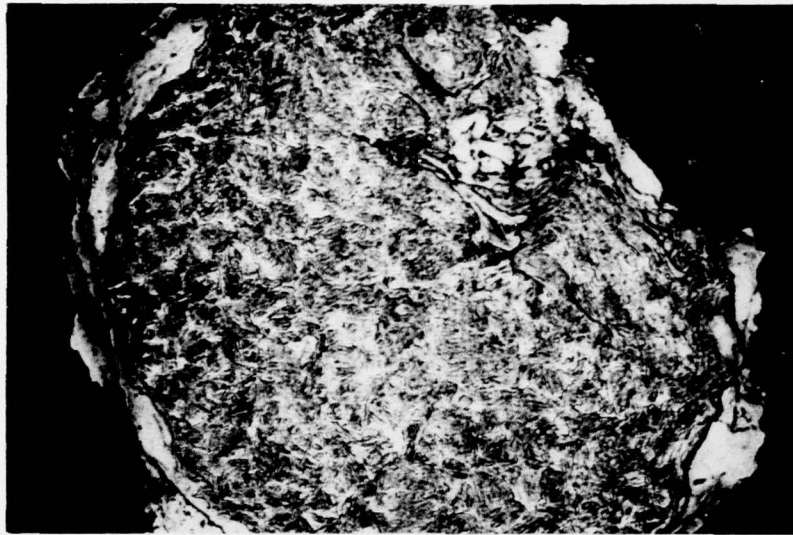


Attriting Run #1
Magnification, 500X

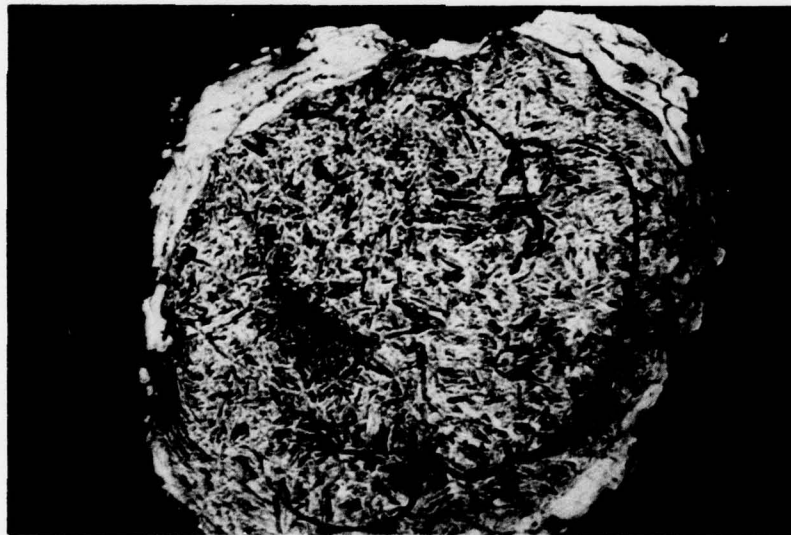


Attriting Run #2
Magnification, 500X

Figure 14. Light photomicrographs of attrited powder particles from attriting runs 1 and 2, etched with nital.

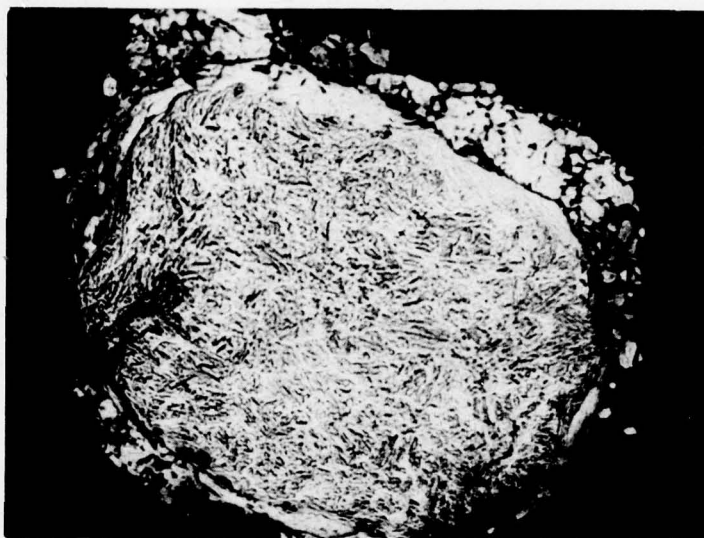


Attriting Run #3
Magnification, 500X

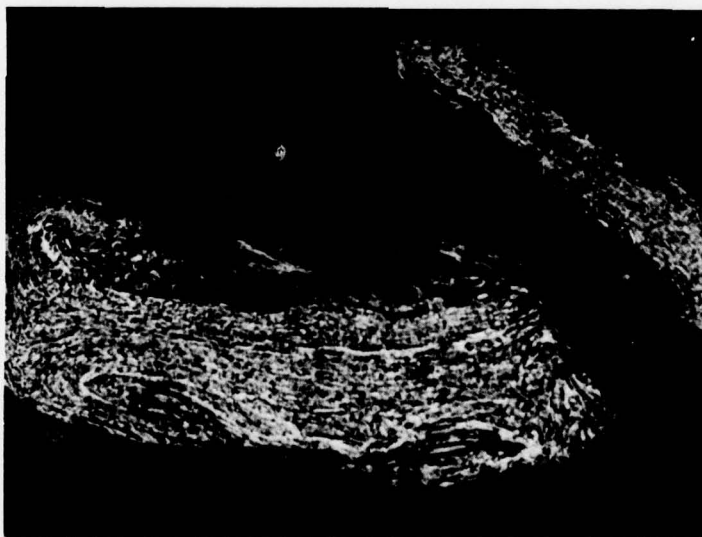


Attriting Run #4
Magnification, 500X

Figure 15. Light photomicrographs of attrited powder particles from attriting runs 3 and 4, etched with nital.



Attriting Run #5
Magnification, 500X



Attriting Run #6
Magnification, 500X

Figure 16. Light photomicrographs of attrited powder particles from attriting runs 5 and 6, etched with nital.

indicating that the attriting process in this run, was effective. Particles from this run are currently being examined by electron microprobe analysis to determine the location of the cerium in the microstructure.

4. Summary and Conclusions

Mechanical alloying experiments were conducted by attriting hydrogen gas atomized 4340 steel powder containing no rare earths with rare earth compound granules in a Szegvari Attritor. Six attriting runs were performed and in five of these runs, cerium or lanthanum was added as 75% cerium - 25% nickel alloy granules or LaNi_5 alloy granules, respectively, at a level equivalent to 0.3 weight percent rare earth content in the starting charge. Rare earth losses of 40 to 70 percent were observed in the attrited powders and these losses were attributed to the small charge size in comparison with the capacity of the attritor tank. The oxygen content of the steel powder increased from 142 ppm to about 2000 ppm during five of the six attriting runs and this increase was attributed to pick-up of residual oxygen in the argon atmosphere used in the attriting operation. The attriting process was not effective in the first five runs, as indicated by only slight deformation of the powder particles. This result was attributed to the hardness of the steel powder particles as a result of rapid cooling during atomization. Annealing of the steel powder prior to attriting in the sixth run resulted in effective attriting, as indicated by heavy deformation of the powder particles. These particles are currently being analyzed in the electron microprobe to determine the extent of mechanical alloying.

C. Rapid Solidification Rate Atomization

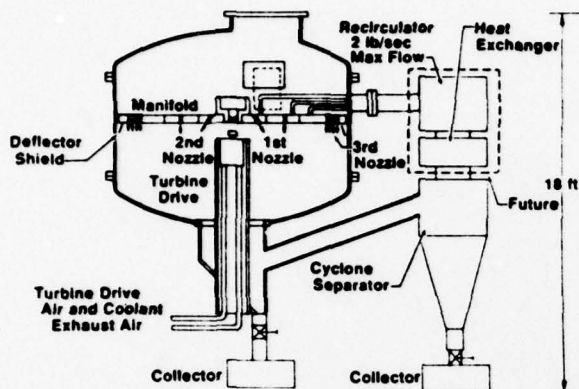
1. Description of Process

The rapid solidification rate or RSR atomization process was developed by Pratt & Whitney Aircraft at their Government Products Division in West Palm Beach, Florida (27-29). This process involves centrifugal atomization of a liquid metal stream combined with forced convective cooling of the atomized droplets/particles using helium gas. The experimental RSR atomization apparatus is illustrated in Figure 17, along with some characteristics of typical powder products. The material to be converted to powder is vacuum induction melted in the upper section of the chamber. When the melt has reached the proper temperature, the chamber is backfilled with helium and the charge poured into the centrally located, preheated tundish. The tundish nozzle then meters the liquid onto the center of the atomizer rotor. The rotor accelerates the liquid to rim speed from the periphery of the rotor. The particles then solidify while traversing the cross flowing helium cooling gas jets. Cooling rates on the order of 10^6 °F/second (5.6×10^5 °K/second) are achieved with this system, and these rates virtually freeze the molten metal into a supersaturated solid solution. The powder yield in the 10 to 100 micron range is about 70 percent of poured weight. Alloy powders based on nickel, cobalt, aluminum, and iron have been made successfully by this process.

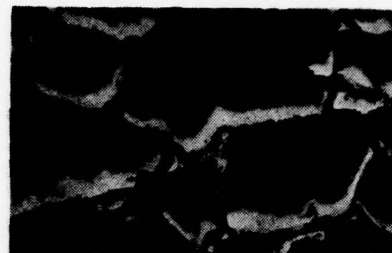
The advantages anticipated in these rapidly solidified powders, aside from greater chemical homogeneity, include (1) an increase in the solubility limits of solute elements, (2) the formation of non-equilibrium structures, (3) large undercooling prior to solidification, and (4) the formation of amorphous structures in certain alloy systems (27-29). Powders produced by the RSR process reveal two distinctly different solidification structures, Figure 17b. The structures were classified as microcrystalline or dendritic, depending on whether or not directionality or secondary arms were present on particle surfaces. Microcrystalline particles did not exhibit directionality and hence were considered to be more homogeneous. It was observed that microcrystalline behavior was exhibited more frequently by smaller particles (less than 20 microns) generally as the result of decreased superheating during atomization (34). The flexibility inherent in this process to increase the size fraction of powders smaller than 20 microns and thus achieve greater numbers of microcrystalline particles offers considerable potential for the development of a new generation of high performance materials. This is the aim of the current research being conducted at Pratt & Whitney Aircraft on RSR powders.

2. Experimental Procedures

A control heat of 4340 steel powder containing no rare earth elements was made by the RSR atomization process, while another RSR heat of 4340 steel powder containing 0.2% cerium is in preparation. Approval to have these heats made at Pratt & Whitney Aircraft, Government Products Division, West Palm Beach, Florida, was obtained from the Tri-Service Committee for DARPA RSR Powder Alloys. Under the DARPA program at Pratt & Whitney Aircraft, RSR powders of various alloys are being produced for interested groups for research purposes.



(a) Experimental rapid solidification rate atomizer.



(b) SEM photographs of microcrystalline (top) and dendritic (bottom) structures found in cross-sections of RSR powder particles.



(c) SEM photograph of MAR-M200 RSR powder particles at 100X.



(d) Internal void in MAR-M200 RSR powder particle at 500X.

Figure 17. Experimental rapid solidification rate atomization unit and some characteristics of typical RSR powder products.

The melt stock for the control heat of RSR powder was obtained from an ingot of vacuum arc remelted 4340 steel. This ingot was machined to the size and shape shown in Figure 18, as required by Pratt & Whitney Aircraft to fit into the melting crucible in their RSR atomization unit. The machined ingot weighed 12.8 lbs. (5.8 kg.). The chemical composition of this ingot is presented in Table 4, along with the composition of the resulting powder. The ingot was converted to RSR powder in the Pratt & Whitney Aircraft AGT 500,000 atomization unit. The alloy was vacuum induction melted in an MgO crucible, and melting was first observed at 2600°F (1700°K). The melt was heated to 2925°F (1880°K), held at that temperature for about 10 minutes, and then transferred through a ceramic nozzle tube to a disk atomizer rotating at 24,000 RPM. Liquid metal droplets were propelled from the atomizer into a helium quench environment with a mass flow rate of approximately 1.0 lb/sec. (0.45 kg./sec.). This operation yielded a total of 12.1 lbs. (5.5 kg.) of powder, including 6.7 lbs. (3.0 kg.) of -140 mesh powder or 55 percent of the total powder yield.

The melt stock for the cerium-bearing heat of RSR powder was obtained by making a 45-pound (20-kg.) ingot of 4340 steel with no rare earth addition, similar to those used for hydrogen gas atomization. This ingot was vacuum-inducted melted and aluminum deoxidized, and cast in the form of a tapered round measuring 4 inches (0.10 m.) in diameter at the bottom, 4-1/2 inches (0.11 m.) in diameter at the top, and 9 inches (0.23 m.) tall. The chemical composition of this ingot is given in Table 4. This ingot was also machined to the size and shape shown in Figure 18. In addition, four holes were drilled in one end of the ingot to accommodate the cerium-nickel alloy additive, in order to ensure thorough mixing of this additive with the molten steel, since the Pratt & Whitney Aircraft AGT 500,000 atomization unit has no facility for adding alloying elements during melting. The four holes were 1/2 inch (0.013 m.) in diameter, 3-1/2 inches (0.089 m.) deep, and equally spaced around a 2-inch (0.051 m.) diameter circle centered about the axis of the ingot. The holes were threaded to a depth of 1/2 inch (0.013 m.) with a 1/2-13 UNC tap. The cerium-nickel additive, in the form of 75% cerium - 25% nickel alloy granules, the same material used for making the cerium additions in the hydrogen gas atomized powders, was poured into the four holes up to the threaded section. Sufficient 75%Ce - 25%Ni was added to obtain a cerium content of 0.2 weight percent in the resulting powder, assuming a cerium recovery of 20 percent, the same degree of recovery that was observed for the hydrogen gas atomized powders. The holes were closed with 1/2-13 UNC by 1/2 inch (0.013 m.) long threaded carbon steel plugs which were tack welded in place to prevent movement. A photograph of the finished ingot is shown in Figure 19. This ingot will also be converted to RSR powder in the Pratt & Whitney Aircraft AGT 500,000 atomization unit.

3. Results and Discussion

Photographs taken in the scanning electron microscope of a sample of the loose powder from the control heat (XSR I-131) of RSR 4340 steel are shown in Figure 20. The powder particles were generally spherical in shape, which is typical of powders made by the RSR atomization process, but approximately 30 percent of the particles were irregular in shape, which is probably the result of collisions with other particles or the chamber walls. There were very few smaller satellite particles attached to the larger particles. In comparison, the hydrogen gas atomized 4340 steel powder particles were generally irregular in shape and had many smaller satellite particles attached to the larger ones (Figure 5). The

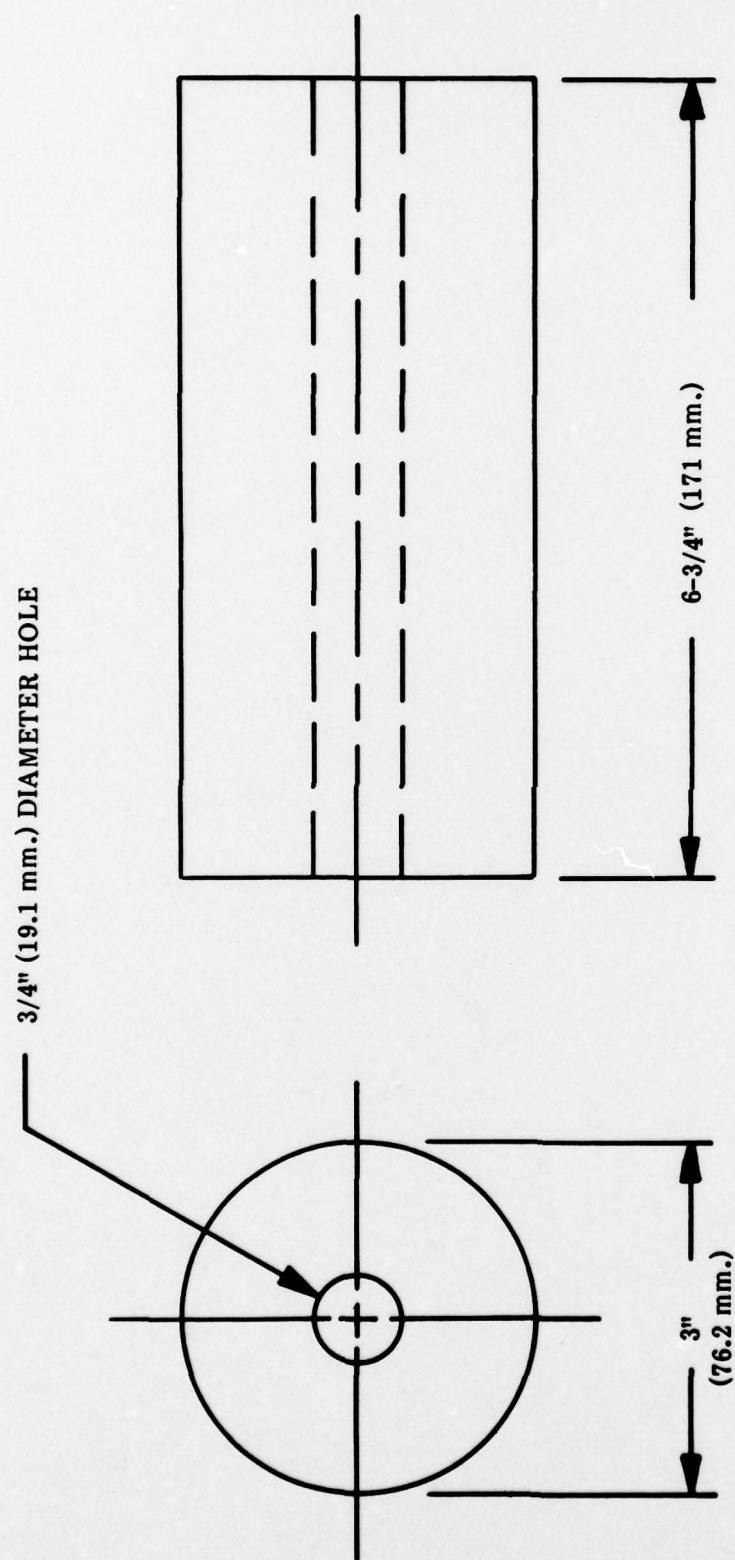
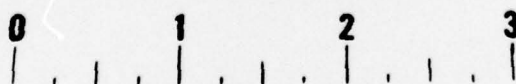


Figure 18. Experimental ingot specified by Pratt & Whitney Aircraft for rapid solidification rate (RSR) atomization.

Table 4
Chemical Compositions of RSR 4340 Steel Ingots
and Powder, Weight Percent

<u>Element</u>	<u>AISI 4340</u> <u>Specification</u>	<u>Control Heat</u>		<u>Ce - Modified Heat</u> <u>Ingot</u>
		<u>Ingot</u>	<u>Powder</u>	
(Heat No.)	-	3824575	XSR I-131	Y627
C	0.38-0.43	0.42	0.42	0.40
Mn	0.60-0.80	0.72	0.60	0.76
P	0.040 max.	0.005	0.011	<0.008
S	0.040 max.	0.003	0.010	0.005
Si	0.20-0.35	0.30	0.34	0.32
Ni	1.65-2.00	1.81	2.07	1.85
Cr	0.70-0.90	0.79	1.08	0.84
Mo	0.20-0.30	0.25	0.27	0.26
Al	-	0.062	0.052	0.043
O	-	-	0.019	-
N	-	-	0.0014	-

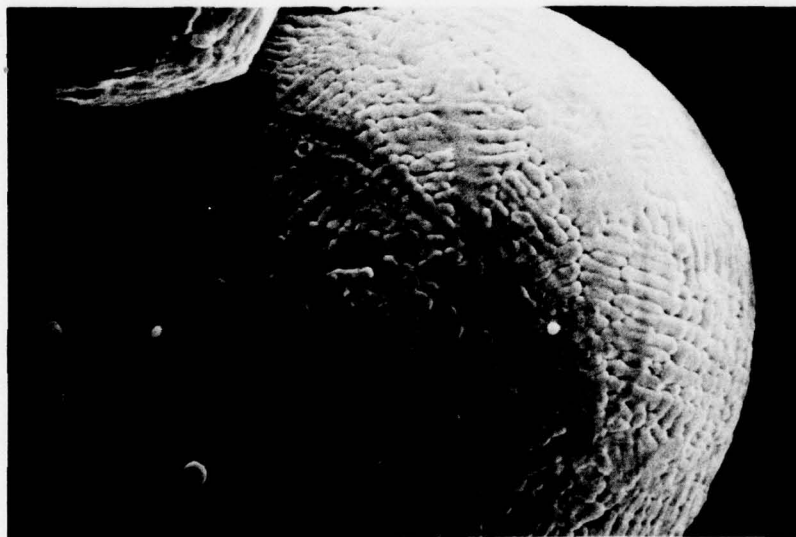


TRW INC.

Figure 19. Photograph of 4340 steel ingot with enclosed Ce-Ni alloy additive, to be atomized by the rapid solidification rate (RSR) process.



Magnification, 100X



Magnification, 1000X

Figure 20. SEM photographs of -140 mesh RSR atomized 4340 steel powder from control heat (XSR I-131) with no rare earth addition.

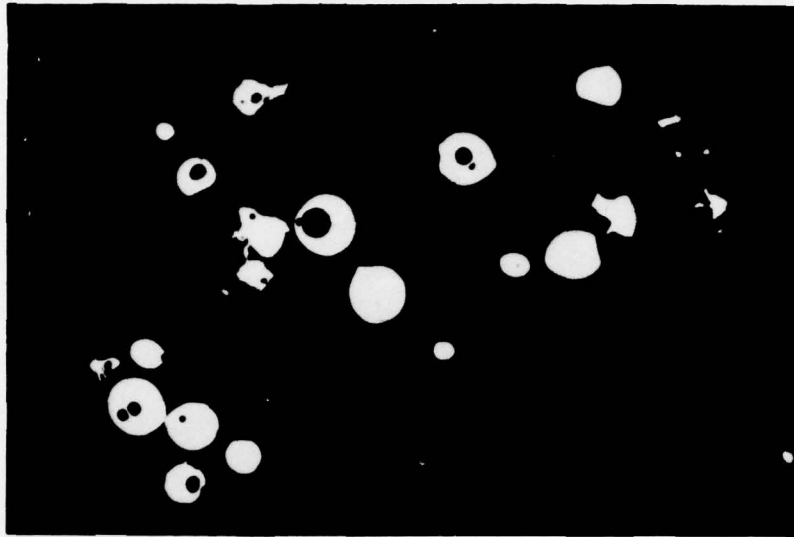
solidification patterns on the surfaces of the RSR powder particles were generally dendritic, as indicated by their striated appearance, whereas those on the surfaces of the hydrogen gas atomized powder particles were equiaxed (Figure 5). These patterns are indicative of a difference in heat flow during atomization of the two types of powders.

Photomicrographs taken in the light microscope of unetched RSR powder particles are shown in Figure 21 and indicate that this powder is clean and relatively free of nonmetallic inclusions, similar to the hydrogen gas atomized 4340 steel powder (Figure 6). However, approximately 50 percent of the RSR powder particles contained internal voids. These voids were probably filled with helium gas, since helium was used for convective cooling in the RSR atomization process. In comparison, the hydrogen gas atomized 4340 steel powder particles contained very few internal voids (Figure 6). Photomicrographs taken in the light microscope of etched RSR and hydrogen gas atomized powder particles are shown in Figure 22. The microstructures of both types of powder consist of untempered martensite, which is typical of quenched 4340 steel. No differences in the microstructures of the two types of powder could be discerned in the light microscope. However, the microstructural analyses of these two types of powder are continuing with metallographic examinations at higher magnifications in the scanning electron microscope.

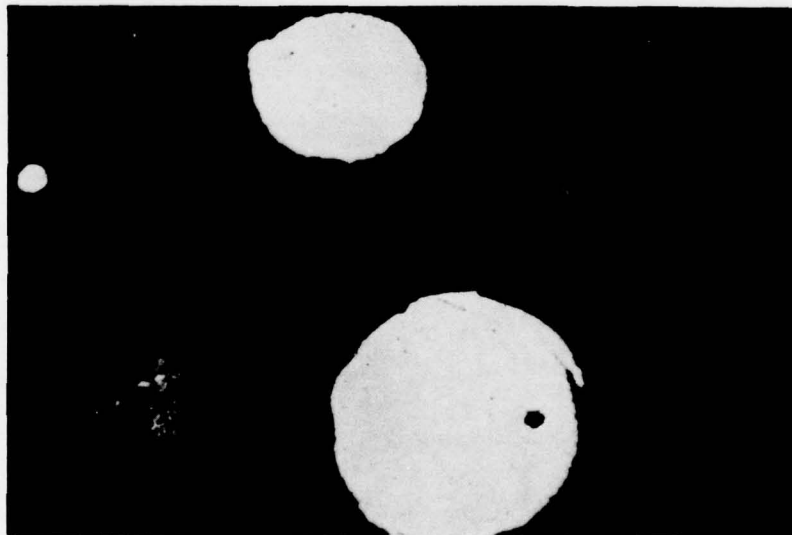
The oxygen content of the control heat of RSR 4340 steel powder was 190 ppm (Table 4), which is slightly higher than that (142 ppm) of the hydrogen gas atomized powder with no rare earth addition (heat X916, Table 1) and somewhat higher than had been expected. The oxygen content of the RSR powder was expected to be less than 100 ppm. The higher oxygen level was probably due to residual oxygen which was present in the helium gas during atomization and was picked up by the steel powder particles.

4. Summary and Conclusions

The rapid solidification rate atomization process developed by Pratt & Whitney Aircraft was employed to make 4340 steel powder. This process utilizes centrifugal atomization of a liquid metal stream and forced convective cooling of the atomized droplets/particles by helium gas to obtain ultrahigh cooling rates and unusual microstructures in the powder particles. A control heat of 4340 steel powder with no rare earth additions was made by the RSR process at Pratt & Whitney Aircraft and an ingot of 4340 steel was prepared for RSR atomization with a 0.2% cerium addition. For the control heat, the RSR process yielded 6.7 lbs. (3.0 kg.) of -140 mesh powder, which was 55 percent of the total powder yield. Scanning electron microscopy of the loose powder showed that the particles were generally spherical in shape, which is typical of powders made by this process, and that the solidification patterns on the particle surfaces were generally dendritic, as compared with those on the surfaces of the hydrogen gas atomized powder particles which were equiaxed. Light microscopy of this powder indicated that it was clean and relatively free of nonmetallic inclusions but contained many internal voids. The microstructure of this powder consisted of untempered martensite, the same as that of the hydrogen gas atomized powders, and no differences in the microstructures of the two types of powder could be discerned by light microscopy. The oxygen content of this powder was 190 ppm, which is higher than had been anticipated (<100 ppm), and this was attributed to pick-up of residual oxygen in the helium gas during atomization. For the cerium-bearing heat, the cerium was added to the melt stock in the form of 75%Ce - 25%Ni alloy granules

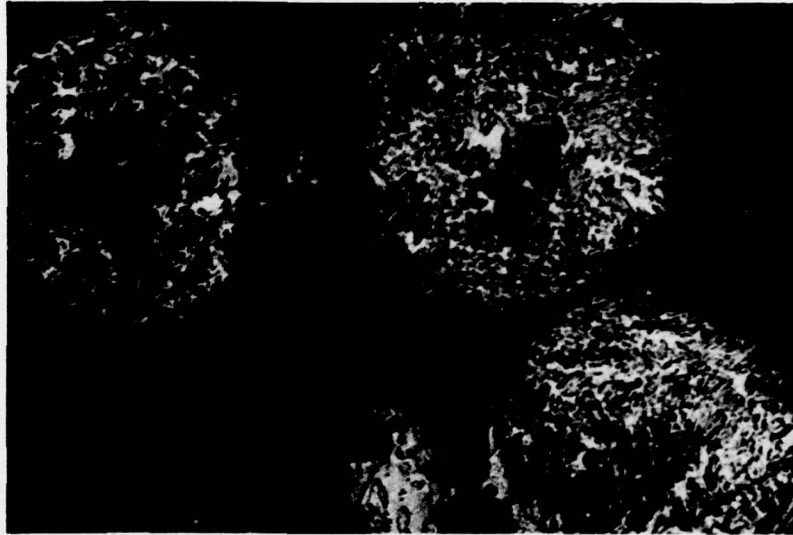


Magnification, 100X

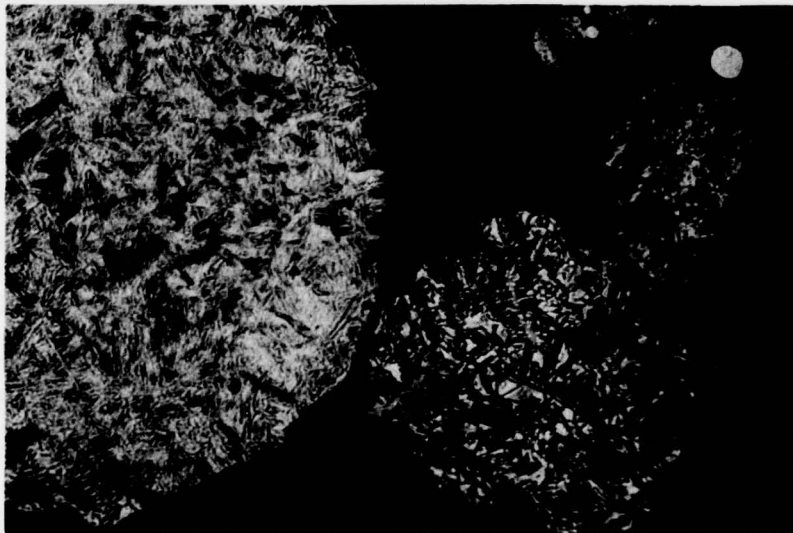


Magnification, 500X

Figure 21. Light photomicrographs of -140 mesh RSR atomized 4340 steel powder from control heat (XSR I-131) with no rare earth addition, unetched.



RSR Atomized Heat XSR I-131
Magnification, 500X



Hydrogen Gas Atomized Heat X916
Magnification, 500X

Figure 22. Light photomicrographs of RSR atomized and hydrogen gas atomized 4340 steel powders, etched with nital.

which were enclosed in holes drilled in one end of the 4340 steel ingot, since alloying elements cannot be added during melting in the RSR atomization unit. The 75%Ce-25%Ni alloy was added at a level sufficient to obtain a cerium content of 0.2 weight percent in the resulting powder with an assumed cerium recovery of 20 percent. This cerium-bearing ingot is to be converted to RSR powder at Pratt & Whitney Aircraft.

IV FUTURE WORK

This program is concerned with the development of powder metallurgy methods for producing rare earth modified high strength 4340 steel with improved resistance to hydrogen embrittlement. The powder metallurgy approach offers a means of obtaining a more uniform distribution of the rare earth elements in the microstructure of the steel, compared with the wrought 4340 steel plate investigated previously, and this improved mechanical properties and hydrogen embrittlement resistance. The work conducted during the first year of the program, which was described in this report, involved studies of material processing techniques for producing rare earth modified 4340 steel from metal powders. In this work, three different methods of making the metal powders were explored: hydrogen gas atomization, mechanical alloying, and rapid solidification rate atomization. During the second year of the program, the material processing studies of the three methods of making the metal powders will be completed and the hydrogen embrittlement resistance of rare earth modified 4340 steel produced from powders made by these three methods will be evaluated. The work planned for the second year is described in the following sections.

A. Powder Production and Characterization

1. Hydrogen Gas Atomization

The first method studied for making rare earth modified 4340 steel powder involved hydrogen gas atomization of 4340 steel prealloyed with cerium by adding a 75% cerium - 25% nickel alloy to the melt. A control heat of hydrogen gas atomized 4340 steel powder with no rare earth addition was also made for comparison purposes, but the yield of useful (-80 mesh) powder from this heat was not sufficient for the planned hydrogen embrittlement evaluation. Therefore, another control heat of 4340 steel powder with no rare earth addition will be made by the hydrogen gas atomization process at Homogeneous Metals, Inc., with argon added to the atomizing gas (50% H_2 + 50%Ar) to increase the yield of -80 mesh powder. Powder from this second control heat will be characterized by chemical and metallographic analyses, including light and scanning electron microscopy. Also, the characterization of powder from the heat of hydrogen gas atomized 4340 steel containing 0.24% cerium (X989) will be completed. This remaining characterization work will include light microscopy, scanning electron microscopy, and electron microprobe analysis. In particular, the electron microprobe analysis will be used to determine the location of the cerium in the microstructure.

2. Mechanical Alloying

The second method studied for making rare earth modified 4340 steel powder involved mechanical alloying of hydrogen gas atomized 4340 steel powder with either 75% cerium - 25% nickel alloy powder or lanthanum-nickel ($LaNi_5$) powder. The characterization of powder from the sixth preliminary attriting run will be completed, since effective attriting occurred in this run, which involved attriting annealed 4340 steel powder with 75% cerium - 25% nickel alloy granules at a level equivalent to 0.3% cerium in the starting charge. This remaining characterization work will include scanning electron microscopy and electron microprobe analysis, with the latter being used specifically to determine the location of the cerium in the microstructure. Three final attriting runs will be made with

sufficient powder (approximately 20 lbs. (9.1 kg.) in each run) for subsequent consolidation, mechanical property evaluation, and hydrogen embrittlement evaluation. In these three runs, the 4340 steel powder will be annealed at 1200°F (920°K) for 2 hours in a vacuum and then attrited with (1) cerium-nickel powder, (2) LaNi₅ powder, and (3) no rare earth addition for control purposes. Three additional heats of hydrogen gas atomized 4340 steel powder containing no rare earths will be made to provide master alloy powder for these three final attriting runs.

3. Rapid Solidification Rate Atomization

The third method studied for making rare earth modified 4340 steel powder consisted of rapid solidification rate atomization of 4340 steel prealloyed with cerium by adding a 75% cerium - 25% nickel alloy to the RSR melt. The characterization of powder from the control heat of RSR atomized 4340 steel powder containing no rare earth elements will be completed. This remaining characterization work will involve scanning electron microscopy of the microstructure of the RSR powder particles to determine how this powder differs from the hydrogen gas atomized 4340 steel powders. The cerium-bearing heat of RSR atomized 4340 steel powder will be made in the AGT 500,000 atomization unit at Pratt & Whitney Aircraft. Powder from this heat will be characterized by chemical and metallographic analyses, including light microscopy, scanning electron microscopy, and electron microprobe analysis. In particular, the scanning electron microscopy will be used to determine how the microstructure of the RSR powder particles differs from that of the hydrogen gas atomized 4340 steel powders and the electron microprobe analysis will be used to determine the location of the cerium in the microstructure.

B. Hot Isostatic Pressing Consolidation

Powders made by all three methods will be consolidated by the hot isostatic pressing process at a high temperature and a high pressure. Seven different types of 4340 steel powder, (1) hydrogen gas atomized powder with and without cerium; (2) attrited powder with cerium, lanthanum, and no rare earths; and (3) rapidly solidified powder with and without cerium, will be consolidated by the HIP process. The HIP temperature will be varied to determine the optimum temperature for obtaining the most favorable compacted microstructure. The as-HIP'ed compacts will then be evaluated metallographically to determine whether a favorable compacted microstructure has been obtained. In addition, the investigation of the cause of failure along the prior particle boundaries in the tensile and Charpy impact tests of the hydrogen gas atomized powder material HIP'ed at 2000°F (1370°K) will be completed, and the HIP process will be modified depending on the results of this investigation, to improve the mechanical properties of the consolidated powders.

C. Evaluation of Powder Processing

The HIP'ed powder metal compacts will be heat treated and then evaluated by light metallography and mechanical property tests which will include tensile and Charpy impact tests conducted at room temperature. Duplicate tensile and Charpy impact tests will be performed on compacts of the seven different types of 4340 steel powder listed in the previous section. The specific processing conditions, particularly the HIP temperature, chosen for this testing will depend on the results of the metallographic analyses of the

HIP'ed compacts. The test specimens will be heat treated to a yield strength level of approximately 200 ksi (1400 MPa) by austenitizing, quenching, and tempering at 450°F (505°K) for comparison with the results obtained previously for rare earth modified wrought 4340 steels (19). In addition, the investigation of the cause of the low ductility and impact resistance of the hydrogen gas atomized powder bar (9G254D), which was HIP'ed at 2000°F (1370°K) and did not exhibit failure along the prior particle boundaries, will be completed. Depending on the results of this investigation, the processing operations will be modified to improve the mechanical properties of the powder metallurgy steels.

D. Selection of Optimum Powder Processing Conditions

The material processing studies will be concluded with the selection of the optimum powder processing conditions. This selection will be made on the basis of the metallographic and mechanical property evaluations of the HIP consolidated powder metallurgy steels. These processing conditions will include attriting parameters and HIP temperature.

E. Hydrogen Embrittlement Evaluation

1. Delayed Failure Testing

The hydrogen embrittlement cracking resistance of the powder metallurgy 4340 steels will be evaluated in this portion of the program. These evaluations will be conducted on steels processed according to four different conditions. Baseline testing will be conducted on steel powders produced without rare earth additions. The other three conditions will be selected on the basis of the studies involving the optimization of processing parameters. It is anticipated that representative material will be selected from rare earth modified hydrogen gas atomized, rapidly solidified and mechanically alloyed powders at a single rare earth content. The optimum powder processing conditions, including attriting time and HIP temperature, established during the processing studies will be used to prepare the test materials. These conditions will be selected on the basis of (1) the resultant homogeneity of the rare earth elements distributed throughout the microstructure and (2) the mechanical property levels established during characterization of Charpy impact and tensile properties of the most promising materials. Prior to hydrogen embrittlement evaluations, however, the material will first be characterized by duplicate tensile and Charpy impact tests conducted on fully heat treated material. These specimens will be heat treated to a yield strength level of approximately 200 ksi (1400 MPa) by austenitizing, quenching and tempering at 450°F (505°K) for comparison with results obtained during the processing parameter study. It is anticipated that a total of eight Charpy impact and eight tensile tests will be conducted during this portion of the program.

The hydrogen embrittlement cracking resistance of the rare earth modified steel powders will be determined by conducting sustained-load delayed failure tests were selected because the entire test system is "closed" with respect to metal-environment interactions, thus minimizing the possible entrance of external hydrogen which could influence the results. Two types of test specimen configurations will be utilized for the delayed failure studies, employing the same specimen preparation procedures as used for the mechanical property screening studies. The specimen configurations include the notch round specimen and the fatigue-precracked, compact tension specimen. A single charging condition selected

on the basis of previous studies at TRW on high strength steel landing gears (35) will be used on these specimens to produce a highly embrittling condition within the steels. Complete delayed failure curves will be obtained for each of the four material conditions selected for the program. It is anticipated that a minimum of 10 specimens will be required for each condition thus resulting in a total of 40 notched round specimens for this portion of the program. A total of 40 compact tension specimens will also be required for this portion of the program.

The results of the delayed failure testing on the powder metallurgy 4340 steel should provide an indication of the effect of hydrogen getter additions on its hydrogen embrittlement resistance compared to the rare earth modified 4340 wrought plate material. If it can be demonstrated that the rare earths increase the crack initiation time or decrease the crack propagation rate in hydrogenated powder metallurgy 4340, then it may also be possible to demonstrate similar benefits in other alloys or specimens exposed to hydrogen containing environments.

2. Hydrogen Content Analysis

The purpose of this portion of the program is to develop an improved understanding of the ability of the rare earth additions to inhibit hydrogen embrittlement in high strength steels produced by powder metallurgy techniques. If it is assumed, for example, that hydrogen trapping or gettering by the rare earth additions is the operative mechanism, once failure has occurred in the hydrogenated and plated specimens, the uncombined hydrogen can diffuse through the matrix and exit through the fresh fracture surface. If the hydrogen has been trapped by the rare earth getters, however, it is unable to diffuse through the metal matrix and remains instead in some combined form within the specimen. The experimental approach to study this possibility will involve obtaining hydrogen contents of specimens after failure. Since all specimens have been charged and plated with the same conditions, the differences in the hydrogen contents may reflect the fact that the rare earth additives have trapped hydrogen, thus reducing its ability to embrittle the material.

The experimental procedure for the hydrogen content measurements will include utilization of the Boeing-developed "Ultra-sensitive Hydrogen Analysis System." This system works on the principle of selective permeation of hydrogen through a semi-permeable metallic membrane. Details regarding operating procedure, range, and accuracy of the instrumentation have been described previously (36). Briefly, specimens are stored in liquid nitrogen immediately after failure to minimize hydrogen loss from the fractured surfaces. Just prior to localized hydrogen measurements on fractured surfaces, the specimens are removed from the liquid nitrogen and thawed at room temperature under blowing dry argon gas. Thereafter, specimens from the desired areas of fractured surfaces are obtained by careful slow cutting of sections under an argon atmosphere, such an operation for high strength steels usually taking about 30 to 45 minutes per sample. For this program, the hydrogen analyses on the fractured surfaces will be carried out in the following three areas for each specimen: (1) fatigue precracked zone, (2) slow crack growth regions, and (3) base metal (a region opposite to the fractured surface, but not including the fractured surface). It is anticipated that a minimum of eight specimens will undergo analysis in this portion of the program. Duplicate specimens will be selected from baseline material as well as rare earth modified hydrogen gas atomized, rapidly solidified and mechanically alloyed powder metallurgy specimens.

3. Metallographic/Fractographic Analysis

The microscopic examination of microstructures associated with failed test specimens and their fracture surfaces is an extremely valuable technique for studying mechanisms of hydrogen-assisted cracking in various materials (37-39). Metallography/fractography has been used extensively to determine how hydrogen and hydrogen-containing environments can influence the microprocesses of crack-tip deformation which in turn control crack propagation. The objective of this part of the program is to ascertain whether the microstructural aspects of the mechanism of hydrogen induced crack growth in powder metallurgy steels are altered by the addition of rare earth elements. In particular, the work will assist in understanding how the more homogeneous distribution of the rare earth additions can effect the hydrogen embrittlement resistance of these materials. In this program, metallographic analyses will be performed using light metallography, the scanning electron microscope and the electron microprobe on the notched round and the compact tension specimens tested under conditions to induce internal hydrogen embrittlement. Fractographic studies will be conducted using the scanning electron microscope. Specimen selection will be made on the basis of the delayed failure results, with representative analyses being made on baseline material and rare earth modified hydrogen gas atomized, rapidly solidified and mechanically alloyed powder metallurgy specimens. It is anticipated that a minimum of 40 specimens will be analyzed in this portion of the program.

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