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ASD-TDR-7-911(III)

## IMPROVED PRODUCTION OF POWDER METALLURGY ITEMS

Interim Technical Documentary Progress Report Nr ASD-TDR-7-911(IE)

1 January 1963 - 31 March 1963

Basic Industry Branch  
Manufacturing Technology Laboratory  
Aeronautical Systems Division  
Air Force Systems Command  
United States Air Force  
Wright-Patterson Air Force Base, Ohio

ASD Project Nr 7-911

This report describes and discusses the results of sintering studies on atomized superalloy powders and on synthesized TZM alloy powders. The time and temperature conditions for optimum sintering are defined, and the metallographic structures of the sintered materials are examined. Also the chemical compositions and gas contents of the alloys are considered in relation to the various stages involved in the manufacture and processing of the superalloys. It is concluded that the boundary conditions for the production of superalloy billets by powder metallurgy techniques are now fairly well established.

(Prepared under Contract AF 33(657)-9140 by Armour Research Foundation, Chicago, Illinois, K. Farrell and N. M. Parikh).

MAY 1 1963

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## FOREWORD

This Interim Technical Documentary Progress Report covers the work performed under Contract AF 33(657)-9140 from 1 January 1963 to 31 March 1963. It is published for technical information only and does not necessarily represent the recommendations, conclusions or approval of the Air Force.

This contract with the Armour Research Foundation, Chicago, Illinois, was initiated under Manufacturing Methods Project 7-911, "Improved Production of Powder Metallurgy Items." It is being accomplished under the technical direction of Mr. G. W. Trickett of the Basic Industry Branch, ASRCTB, Manufacturing Technology Laboratory, Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio.

Dr. N. M. Parikh of the Foundation's Metals and Ceramics Division is the engineer in charge. Others who cooperated in the research and in the preparation of the report were Dr. K. Farrell, Associate Metallurgist and Mr. C. Carter, Assistant Metallurgist. This report has been given the internal designation ARF-B247-9.

The primary objective of the Air Force Manufacturing Methods Program is to develop on a timely basis manufacturing processes, techniques and equipment for use in economical production of USAF materials and components. The program encompasses the following technical areas:

Rolled Sheet, Forgings, Extrusions, Castings, Fiber and Powder Metallurgy; Component Fabrication, Joining, Forming, Materials Removal; Fuel, Lubricants, Ceramics, Graphites, Nonmetallic Structural Materials; Solid State Devices, Passive Devices, Thermionic Devices.

Your comments are solicited on the potential utilization of the information contained herein as applied to your present or future production programs. Suggestions concerning additional Manufacturing Methods development required on this or other subjects will be appreciated.

ABSTRACT - SUMMARY  
Interim Technical Documentary Report

ASD-TDR-7-911(III)  
March 1963

## IMPROVED PRODUCTION OF POWDER METALLURGY ITEMS

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N. M. Parikh  
Armour Research Foundation

This report describes and discusses the results of sintering studies on atomized superalloy powders and on synthesized TZM alloy powders. The time and temperature conditions for optimum sintering are defined, and the metallographic structures of the sintered materials are examined. Also the chemical compositions and gas contents of the alloys are considered in relation to the various stages involved in the manufacture and processing of the superalloys. It is concluded that the boundary conditions for the production of superalloy billets by powder metallurgy techniques are now fairly well established.

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## IMPROVED PRODUCTION OF POWDER METALLURGY ITEMS

### I. INTRODUCTION

This is the third Quarterly Report on the subject program and covers the work done in the period 1 January 1963 to 31 March 1963. The results herein are concerned with the development of optimum sintering conditions in the three atomized superalloys (Inco 713C, Udimet 700, and PH15-7Mo) and in synthesized TZM alloys, and with the metallography of the sintered materials so produced. In addition, some data are included on chemical analyses of the superalloy sinters at various stages in their manufacture. Also, some further density measurements have been made on the atomized powders and some compaction tests on the TZM alloys.

### II. RESULTS AND DISCUSSION

#### A. Further Density and Compactibility Tests on the Powders

Some apparent density and compactibility measurements on atomized superalloy powders were given in Interim Technical Documentary Progress Report Nr ASD-TDR-7-911(II). Further data have since been collected on the atomized powders and on the synthesized TZM powder.

The sieve analyses and flowabilities of the -80 mesh powders from the three latest superalloy melts are given in Table I, and the apparent densities of the powders are plotted in Figures 1(a) and (b). Figure 1(a) shows the apparent densities as a function of the graded particle sizes, the densities increasing with decreasing particle size. The apparent densities of the as-made, mixed powders from which the coarser size fractions were progressively removed are plotted in Figure 1(b). Here it can be seen that as the powders become finer, the densities remain almost constant at the levels of the -325 mesh powders, or tend to decrease slightly towards the -325 mesh values. The differences between the (a) and (b) Figures are a result of the interstices, or voids, between the powder particles. The total

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TABLE I

SIEVE ANALYSES AND FLOWABILITIES  
OF ATOMIZED SUPERALLOY POWDERS (-80 mesh)

| Material   | Melt<br>No. | Sieve Analysis, wt% |               |               |               |      | Flowability,<br>sec. |
|------------|-------------|---------------------|---------------|---------------|---------------|------|----------------------|
|            |             | -80/<br>+140        | -140/<br>+200 | -200/<br>+270 | -270/<br>+325 | -325 |                      |
| Inco 713C  | 15          | 27.4                | 23.2          | 23.1          | 7.2           | 19.1 | 21.3                 |
| Udimet 700 | 4           | 28.8                | 21.7          | 23.0          | 7.3           | 19.2 | 21.7                 |
| PH15-7Mo   | 7           | 20.2                | 21.4          | 24.6          | 8.4           | 25.4 | 19.6                 |

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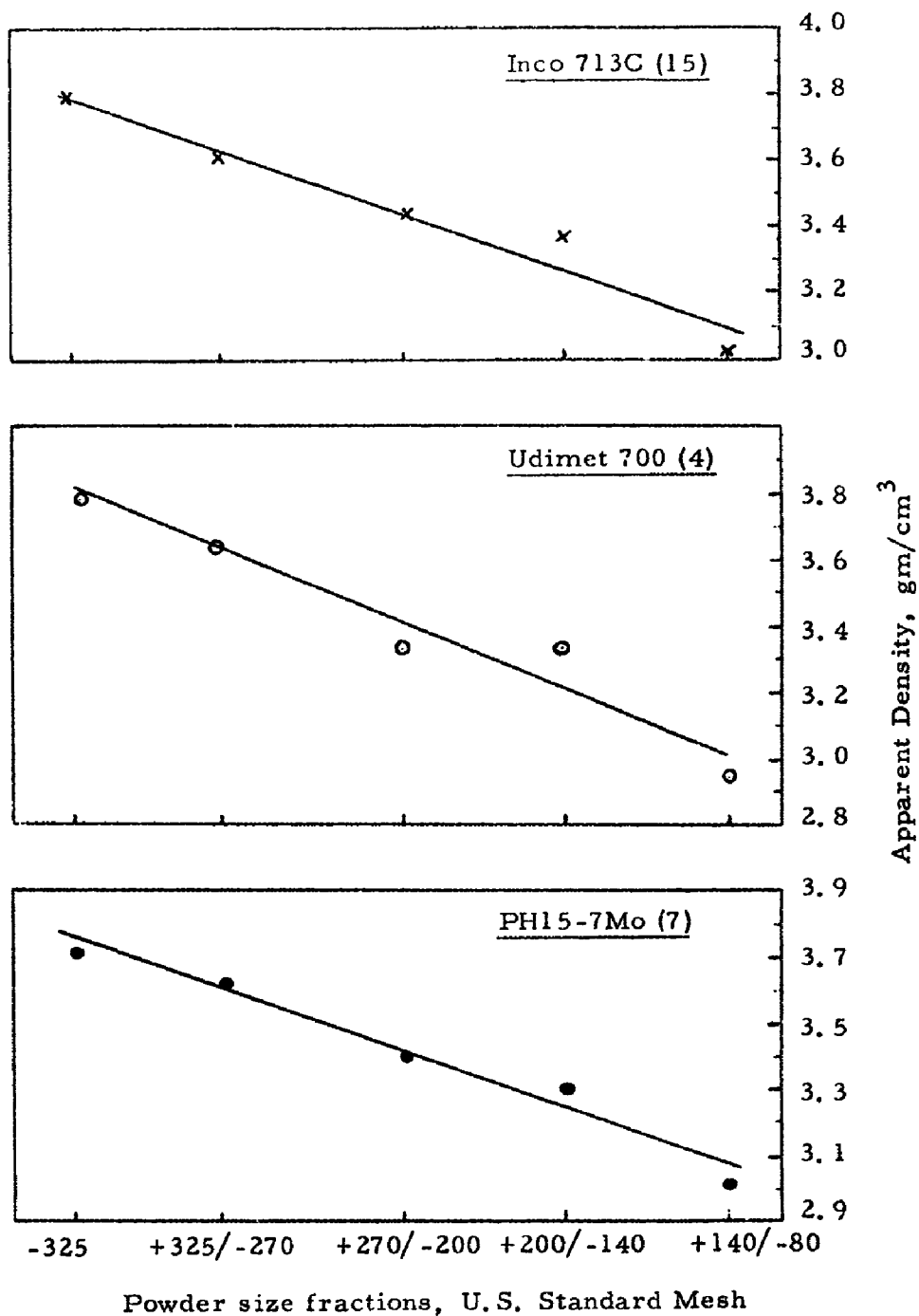


FIG. 1 (a) - Apparent Densities of Loose Superalloy Powders as a Function of Powder Particle Size.

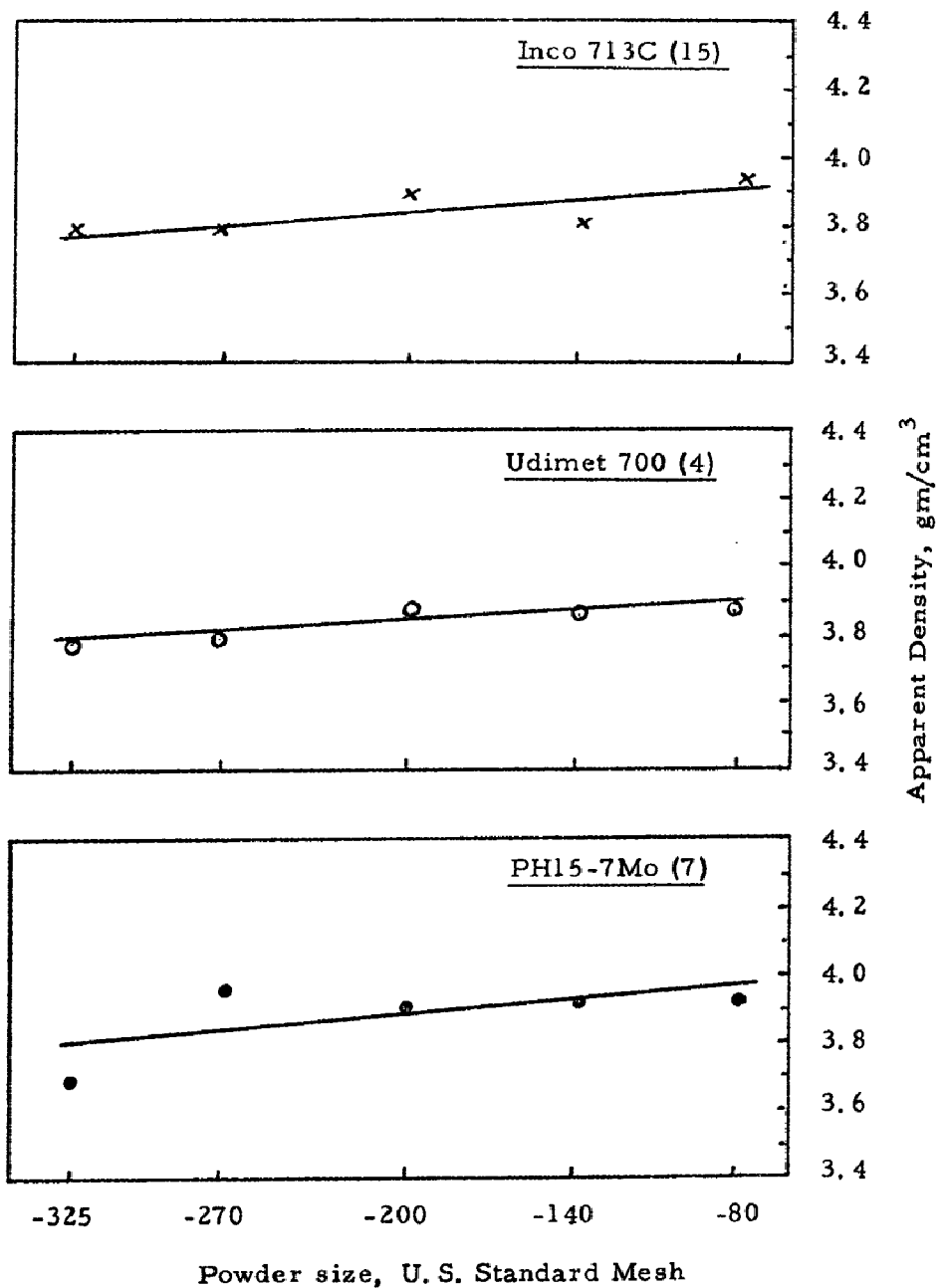


FIG. 1(b) - Apparent Densities of Loose As-made Powders.

volume of these voids is clearly a minimum in the -80 mesh powders. Since sintering is simply a means of eliminating these voids, sintering should be easier in the -80 mesh powder than in any of the graded particle fractions. Also, the -80 mesh powder should give the greatest densification on compaction. Moreover, the ratios of the theoretical densities of the alloys (Inco 713C--7.70 gm/cc, Udimet 700--7.65, PH15-7Mo--7.72) to the apparent densities of the -80 mesh powders are less than two to one, an indication that the powders should be easily manageable with ordinary compaction techniques. This is born out by the compaction tests reported in the previous Quarterly Report.

The apparent densities of a synthesized TZM powder mix containing a nominal 0.1% carbon are shown in Figure 2, and the compactabilities of two size grades of the powder are demonstrated in Figure 3. The apparent densities follow the same pattern as those of the atomized powders in Figure 1(b) and the same considerations apply. The powder compacts have good green strengths and can be handled easily.

#### B. Chemical Analyses and Gas Contents

The gas contents of the atomized superalloy powders as a function of powder particle size are reproduced in Figure 4. The marked dependence of oxygen content on particle size at the smaller particle sizes suggests that, in the finer powder at least, the oxygen is largely on the surface of the powders; that is, it is adsorbed during atomization. This is confirmed by the fact that the oxygen contents of the finer powders may be very high (as great as 0.5%) if the atomizer tank is not flushed with argon just prior to atomization. In the larger particle sizes the oxygen contents become independent of particle size; this would seem to indicate appreciable oxygen in solution in the metal.

In the Inco 713C and Udimet 700 powders the nitrogen contents are low, but there is considerable nitrogen absorption by the PH15-7Mo powder. The nitrogen contents of all three metal powders show much less dependence on powder size than do the oxygen contents, which suggests that the nitrogen must be in solution in the metal. The high nitrogen content of the PH15-7Mo powder was originally thought to be due to a high

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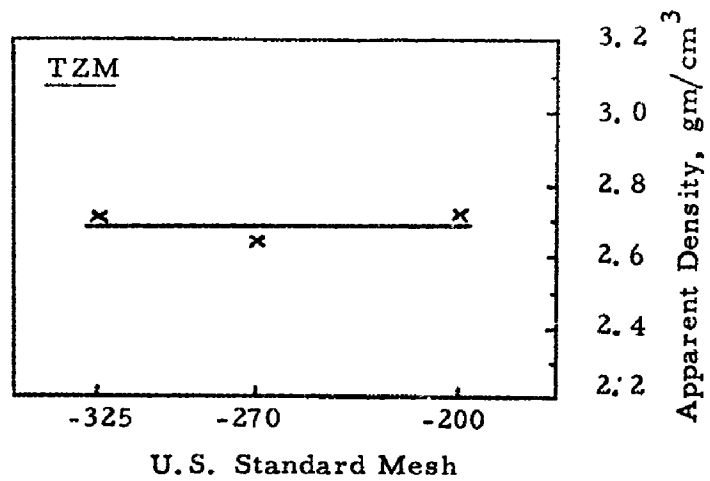


FIG. 2 - Apparent Densities of TZM Powder Mix Containing 0.1% Carbon.

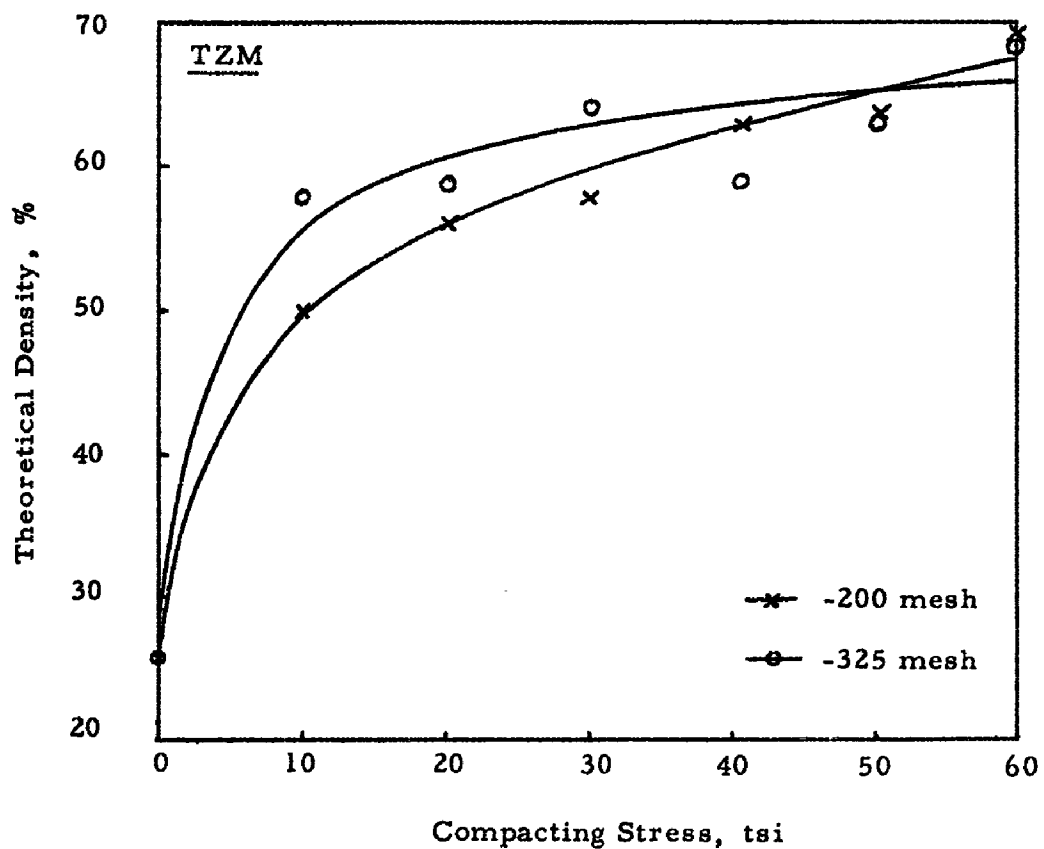


FIG. 3 - Compactibility Tests on TZM Powder Mix Containing 0.1% Carbon.

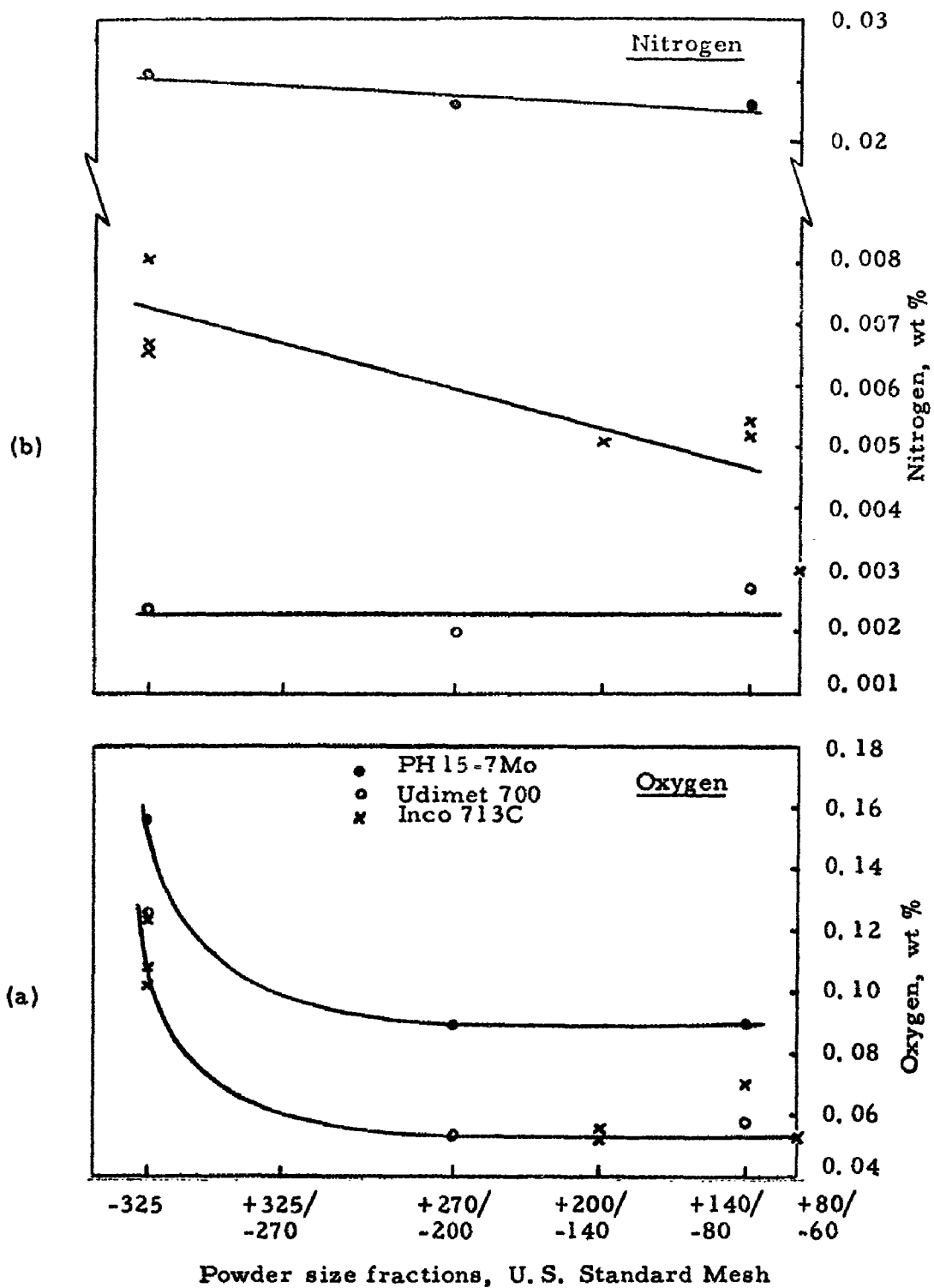


FIG. 4 -Gas Contents of Atomized Powders as a Function of Powder Particle Size.

nitrogen content in the as-received melt stock, but analysis of the melt stock indicates that this is not so. Table II gives the gas contents of the melt stock and of powders atomized from this stock and shows clearly that in PH15-7Mo powders the oxygen and nitrogen contents do not originate from the melt stock. It is also evident from Table II that there is very little nitrogen pick-up by the Inco 713C and Udimet 700 powders.

The acceptable upper limit of nitrogen in Inco 713C and Udimet 700 powders is set at 0.005 wt%, and that in PH15-7Mo powder at 0.02 wt%. No oxygen specification is laid down but it would seem that 0.10 wt% maximum would be satisfactory. An examination of Table II reveals that the -80 mesh powders of Inco 713C and Udimet 700 alloys easily meet the gas content requirements, but the PH15-7Mo alloy is a borderline case. It must be pointed out, however, that PH15-7Mo has a higher melting temperature than the other two alloys and in our apparatus took much longer to melt than the other alloys. Even though an argon blanket was used during melting, the top of the melting pot could not be sealed completely and some air could leak into the pot. The longer exposure of the PH15-7Mo during melting would greatly enhance gas pick-up in this alloy, especially since PH15-7Mo is an iron-base alloy and will have a high affinity for oxygen and nitrogen.

Some gas pick-up may be expected in all the alloys during atomization because, although the atomizer tank was prepurged with argon, this served only to dilute the air in the tank and did not wholly eliminate it. The significance of these results is that they were obtained on materials produced under conditions in which only the most elementary anti-gas precautions were applied, and yet in two out of the three cases the gas contents were well within the specifications. More stringent measures should give much lower gas contents.

An attempt to determine the relative influences of melting, atomizing, and sintering on the gas contents of the superalloys produced the gas analyses in Table III. At first glance it seems that there are some large discrepancies between these analyses and those in Table II. For example, if the oxygen contents of the melt stock are compared with those

TABLE II  
GAS CONTENTS OF SUPERALLOY MELT STOCK  
AND -80 MESH ATOMIZED POWDERS

| Material                         | Oxygen, wt% | Nitrogen, wt% |
|----------------------------------|-------------|---------------|
| Inco 713C (melt stock)           | 0.0138      | 0.0030        |
| Inco 713C (11) (-80 mesh powder) | 0.069       | 0.0036        |
| Udimet 700 (melt stock)          | 0.031       | 0.0010        |
| Udimet 700 (1) (-80 mesh powder) | 0.079       | 0.0018        |
| PH15-7Mo (melt stock)            | 0.004       | 0.0050        |
| PH15-7Mo (1) (-80 mesh powder)   | 0.097       | 0.0213        |

TABLE III

GAS CONTENTS OF SUPERALLOYS BEFORE AND AFTER  
MELTING, AFTER ATOMIZATION, AND AFTER SINTERING

| Alloy                                      | Oxygen, wt%     | Nitrogen, wt% |
|--------------------------------------------|-----------------|---------------|
| <u>Inco 713C</u>                           |                 |               |
| Melt stock                                 | 0.0437 (0.0138) | 0.0015        |
| As-melted (melt 15)                        | 0.0146          | 0.0115        |
| As-atomized (-80 mesh powder)<br>(melt 15) | 0.1520          | 0.0128        |
| As-sintered* (melt 15)                     | 0.1500          | 0.0042        |
| <u>Udimet 700</u>                          |                 |               |
| Melt stock                                 | 0.125 (0.031)   | 0.0054        |
| As-melted (melt 4)                         | 0.0307          | 0.0040        |
| As-atomized (-80 mesh powder)<br>(melt 4)  | 0.0669          | 0.0039        |
| As-sintered* (melt 4)                      | 0.0650          | 0.0014        |
| <u>PH15-7Mo</u>                            |                 |               |
| Melt stock                                 | 0.106 (0.004)   | 0.0062        |
| As-melted (melt 7)                         | 0.0218          | 0.0651        |
| As-atomized (-80 mesh powder)<br>(melt 7)  | 0.149           | 0.0850        |
| As-sintered* (melt 7)                      | 0.200           | 0.0042        |

\* Sintering conditions:

|            |    |                                |
|------------|----|--------------------------------|
| Inco 713C  | -- | 1 1/2 hrs at 1300°C in vacuum. |
| Udimet 700 | -- | 1 1/2 hrs at 1250°C in vacuum. |
| PH15-7Mo   | -- | 1 1/2 hrs at 1440°C in argon.  |

of the melt stock in Table II (in parentheses in Table III), they are seen to be greater by factors of between 3 and 25. The two sets of samples were taken from the same casts of vacuum-melted material and should therefore have the same low gas contents. However, solid samples were used for the analyses in Table II, whereas the melt stock values in Table III were determined on turnings. If it is reasonable to suppose that the true oxygen contents of the melt stock are consistently low, then the apparent discrepancies may well be due to the differences in surface areas of the samples and hence to the amount of gas adsorbed on the surfaces of the samples.

In keeping with this view and with the previous postulate that nitrogen may be in solution in the metal and not adsorbed on the metal surface, it should be noted that the variation in nitrogen contents between the melt-stock figures in Tables II and III is small.

The problem of surface-adsorbed gases cannot be emphasized too strongly since it is important to realize that even the cleanest-looking samples may adsorb gases in proportion to their surface area even at room temperature. This implies that even if every precaution were taken to prevent gas adsorption during atomization, some gas pick-up might be expected during processing of the powders.

If the melt-stock analyses in Table III are replaced by the more acceptable oxygen values from Table II, we can obtain a general picture of the variation in gas contents during the processes of melting, atomizing, and sintering. On this basis, the melting process has little influence on the oxygen content of Inco 713 and Udimet 700 but markedly increases that of PH15-7Mo; atomizing causes large increases in oxygen in Inco 713C and PH15-7Mo but has only a small influence on Udimet 700; sintering has little or no effect on the oxygen content of the Inco 713C and Udimet 700 powders, which were sintered in vacuum, but appears to have raised that of PH15-7Mo, which was sintered in argon.

Dealing now with nitrogen contents it is found that melting does not change the nitrogen content of Udimet 700 but strongly increases that of Inco 713C and PH15-7Mo; on atomizing, there is little change in

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the as-melted nitrogen contents of all the alloys, thus confirming the view that nitrogen is in the metal rather than on the powder surfaces. On sintering, the nitrogen contents of all the alloys fall to approximately the levels of the melt stocks. This indicates that the nitrogen is less tightly bound up in the metals than is the oxygen and suggests that nitrogen should give little trouble in sintered powder compacts. However, some difficulties may be experienced from oxygen, but these can be minimized by rigid control of melting furnace and atomizer tank atmospheres so that oxygen is eliminated.

The chemical analyses of the three superalloys in the as-received, as-melted, as-atomized, and as-sintered conditions are given in Table IV. In most cases only the major elements have been determined. There are some small differences in the concentrations of some of these elements, differences which when they show an increase in concentration can probably be attributed to errors in the analyses, but for the most part there is little change brought about by melting, atomizing, or sintering. The biggest changes are the reduction of the carbon and aluminum contents of the PH15-7Mo on melting and the fall in the titanium contents of the Inco 713C and the Udimet 700 on melting. However, these changes are not considered significant, and it can be said that processing has induced no major changes in the chemical compositions of the three superalloys.

The chemical specification of the TZM alloy is given in Table V. There is an error in the fifth Letter Report on the subject program (Table II) in which the carbon content of TZM alloy is incorrectly quoted as 0.09%. TZM alloy is not prepared by atomization but is synthesized from molybdenum powder. The molybdenum is first mixed with predetermined amounts of zirconium hydride and titanium hydride, and the mixture is decomposed by heating in argon at 600°C. This gives a molybdenum-titanium-zirconium alloy free from hydrogen. Carbon is added in the form of fine graphite. The mixture is ball-milled and the final mix is compacted and sintered. Since some carbon loss was expected during sintering, three alloys were prepared containing initial carbon contents of 0.1, 0.3, and 0.5%C. The chemical analyses of these alloys, after being sintered for 6 hr at 2000°C in vacuo, are presented in Table V.

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**TABLE IV**  
**INFLUENCE OF MELTING, ATOMIZATION AND SINTERING**  
**ON CHEMICAL COMPOSITION OF SUPERALLOYS**

| Alloy                | C     | Mn    | Si    | Cr    | Ni   | Mo   | Al   | Cb + Ta | Cu    | S      | Zr   | Fe    | Ti   | Bo     | Co     |
|----------------------|-------|-------|-------|-------|------|------|------|---------|-------|--------|------|-------|------|--------|--------|
| <u>Inco 713C</u>     |       |       |       |       |      |      |      |         |       |        |      |       |      |        |        |
| Melt stock           | 0.044 | <0.10 | 0.23  | 13.06 | Bal. | 4.17 | 5.65 | 2.58    | <0.05 | <0.015 | 0.09 | 1.39  | 0.94 | 0.010  | <0.010 |
| As-melted (15)       | 0.03  | --    | --    | 13.27 | Bal. | 4.05 | 5.63 | 2.23    | --    | --     | 0.04 | 1.58  | 0.74 | <0.010 | --     |
| -80 mesh powder (15) | 0.04  | --    | --    | 13.63 | Bal. | 4.50 | 5.23 | 2.17    | --    | --     | 0.10 | 1.25  | 0.72 | <0.010 | --     |
| As-sintered (vacuum) | 0.05  | --    | --    | 13.12 | Bal. | 4.65 | 6.70 | 2.13    | --    | --     | 0.08 | 1.26  | --   | --     | --     |
| <u>Udimet 700</u>    |       |       |       |       |      |      |      |         |       |        |      |       |      |        |        |
| Melt stock           | 0.06  | 0.17  | <0.03 | 16.03 | Bal. | 5.42 | 4.05 | --      | --    | 0.010  | --   | <0.05 | 3.53 | 0.13   | 18.42  |
| As-melted (4)        | 0.14  | --    | --    | 15.90 | Bal. | 4.60 | 4.10 | --      | --    | --     | --   | 0.43  | 3.10 | 0.08   | 18.96  |
| -80 mesh powder (4)  | 0.05  | --    | --    | 15.82 | Bal. | 5.00 | 3.61 | --      | --    | --     | --   | 0.29  | 3.15 | 0.08   | 18.01  |
| As-sintered (vacuum) | 0.08  | --    | --    | 15.82 | Bal. | 5.30 | 4.26 | --      | --    | --     | --   | 0.23  | 3.25 | 0.06   | 17.80  |
| <u>PH15-7Mo</u>      |       |       |       |       |      |      |      |         |       |        |      |       |      |        |        |
| Melt stock           | 0.07  | <0.20 | 0.19  | 15.70 | 7.00 | 2.55 | 1.05 | --      | --    | <0.030 | --   | Bal.  | --   | --     | --     |
| As-melted (7)        | 0.03  | --    | --    | 15.64 | 7.41 | 2.65 | 0.86 | --      | --    | --     | --   | Bal.  | --   | --     | --     |
| -80 mesh powder (7)  | 0.02  | --    | --    | 15.54 | 7.40 | 2.70 | 0.76 | --      | --    | --     | --   | Bal.  | --   | --     | --     |
| As-sintered (argon)  | 0.02  | --    | --    | 15.52 | 7.54 | 2.00 | 0.80 | --      | --    | --     | --   | Bal.  | --   | --     | --     |

TABLE V

CHEMICAL ANALYSES OF SYNTHESIZED TZM ALLOYS

| C                               | Zr   | Ti   | Mo   | O         | N          |
|---------------------------------|------|------|------|-----------|------------|
| <u>Alloy Specification, wt%</u> |      |      |      |           |            |
| 0.02                            | 0.1  | 0.5  | Bal. | 0.005 max | Not stated |
| <u>Nominal 0.1%C Mix</u>        |      |      |      |           |            |
| 0.0061                          | 0.09 | 0.47 | Bal. | 0.163     | 0.0037     |
| <u>Nominal 0.3%C Mix</u>        |      |      |      |           |            |
| 0.0057                          | 0.10 | 0.47 | Bal. | 0.0448    | 0.0039     |
| <u>Nominal 0.5%C Mix</u>        |      |      |      |           |            |
| 0.0064                          | 0.10 | 0.46 | Bal. | 0.0571    | 0.0139     |

The zirconium and titanium contents are highly satisfactory, but the carbon contents are well below the specification. Also the oxygen contents are high; this suggests an explanation of the large carbon losses. It is suspected that the fine molybdenum powder particles have oxidized surfaces, and that during sintering the graphite reduces these oxide films and is evolved into the vacuum as an oxide of carbon. There is some evidence in Table V that tends to support this hypothesis; in those mixes containing initially 0.3 and 0.5%C the oxygen contents are much lower than that in the 0.1%C mix. Therefore, to obtain the required carbon content in the sintered powders, the oxide films must be reduced before the final graphite addition is made. Some experiments are now being carried out in this direction. The molybdenum-titanium-zirconium alloy powder is being mixed with measured amounts of graphite and heated in vacuo at 1000°C. Chemical analyses will reveal the amount of graphite necessary to reduce the oxygen content to a minimum and to retain the required carbon in the mix.

#### C. Sintering Data

The initial sintering data were reported in Interim Technical Documentary Progress Report No. ASD-TDR-7-911(II), where it was pointed out that the PH15-7Mo powder compacts refused to sinter in a vacuum. This was believed due to the evolution of a volatile component from the alloy. Subsequent investigation has revealed that the PH15-7Mo alloy sinters easily in argon. In Figure 5 the previous results are produced together with the more recent findings. The sintering temperatures for the PH15-7Mo alloy are considerably higher than those for the other two atomized alloys. The plateau in the PH15-7Mo curve at about 85% theoretical density persists in both vacuum-sintered and argon-sintered specimens, after which the shape of the curve follows an upward path parallel to those of the other two alloys.

The above curves were the results of 1 hr sintering treatments at different temperatures. The influence of time of sintering on the atomized powders at several temperatures is shown in Figures 6 to 8, and on TZM powders in Figure 9. There are some apparent discrepancies between the data in Figure 5 and those in Figures 6 and 7 that still require explanation.

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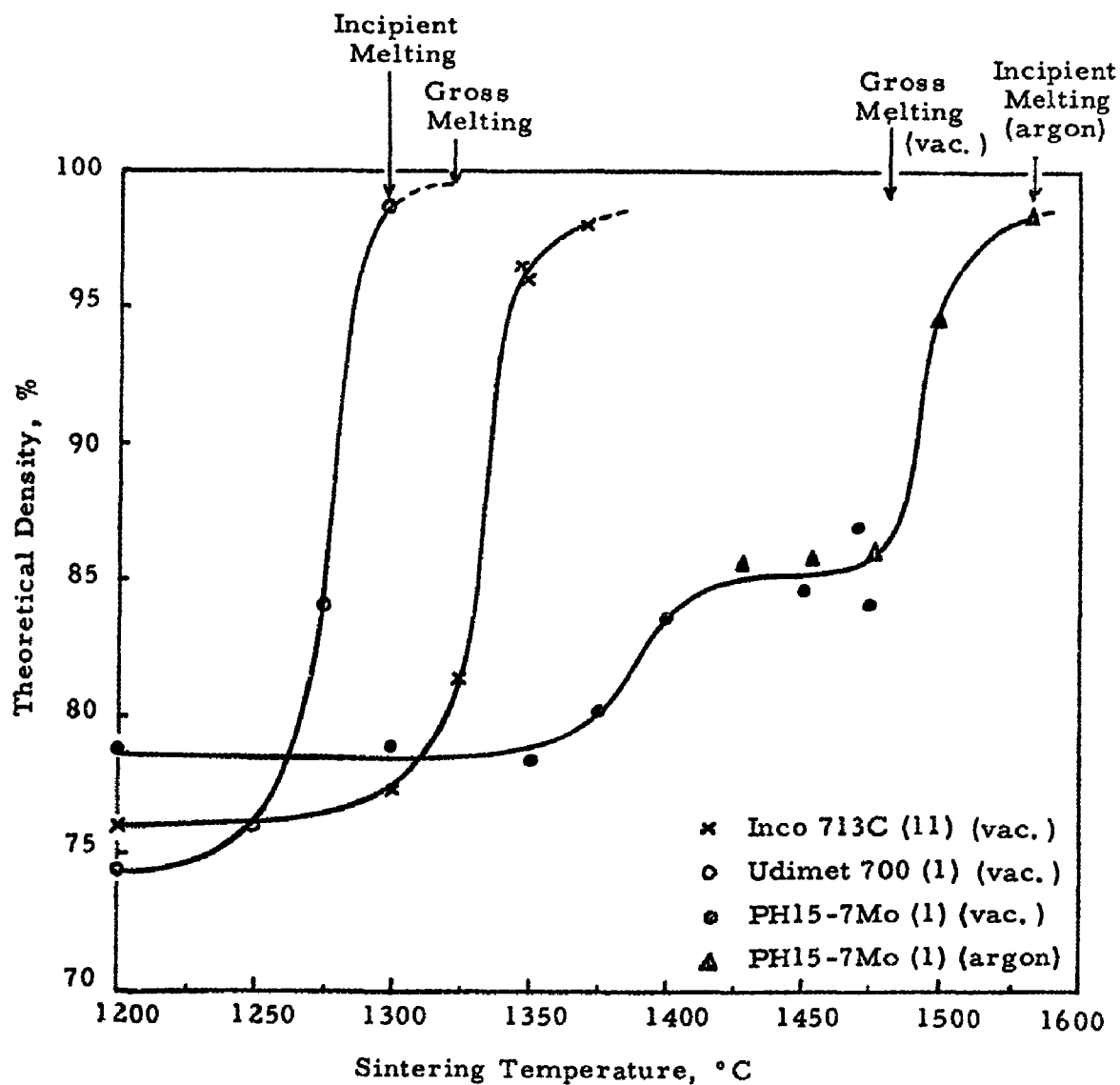


FIG. 5 - Sintering Tests on -80 Mesh Powder Compacts. Specimens Held at Temperature in Argon or in Vacuum (~0.1 micron) for 1 hour.

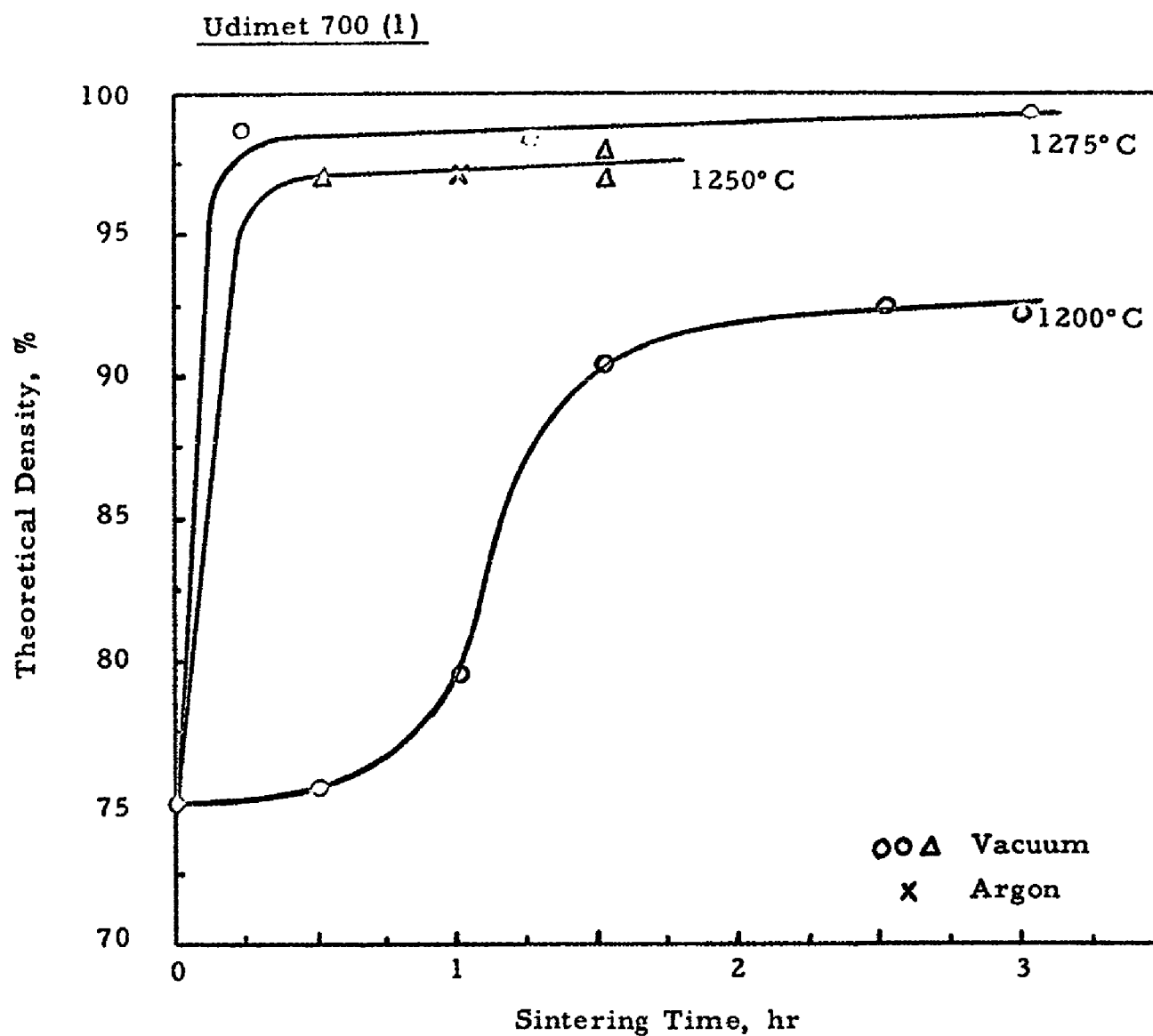


FIG. 6 - Influence of Sintering Time at Several Temperatures on the Density of Udimet 700 Atomized Powder Compacts.

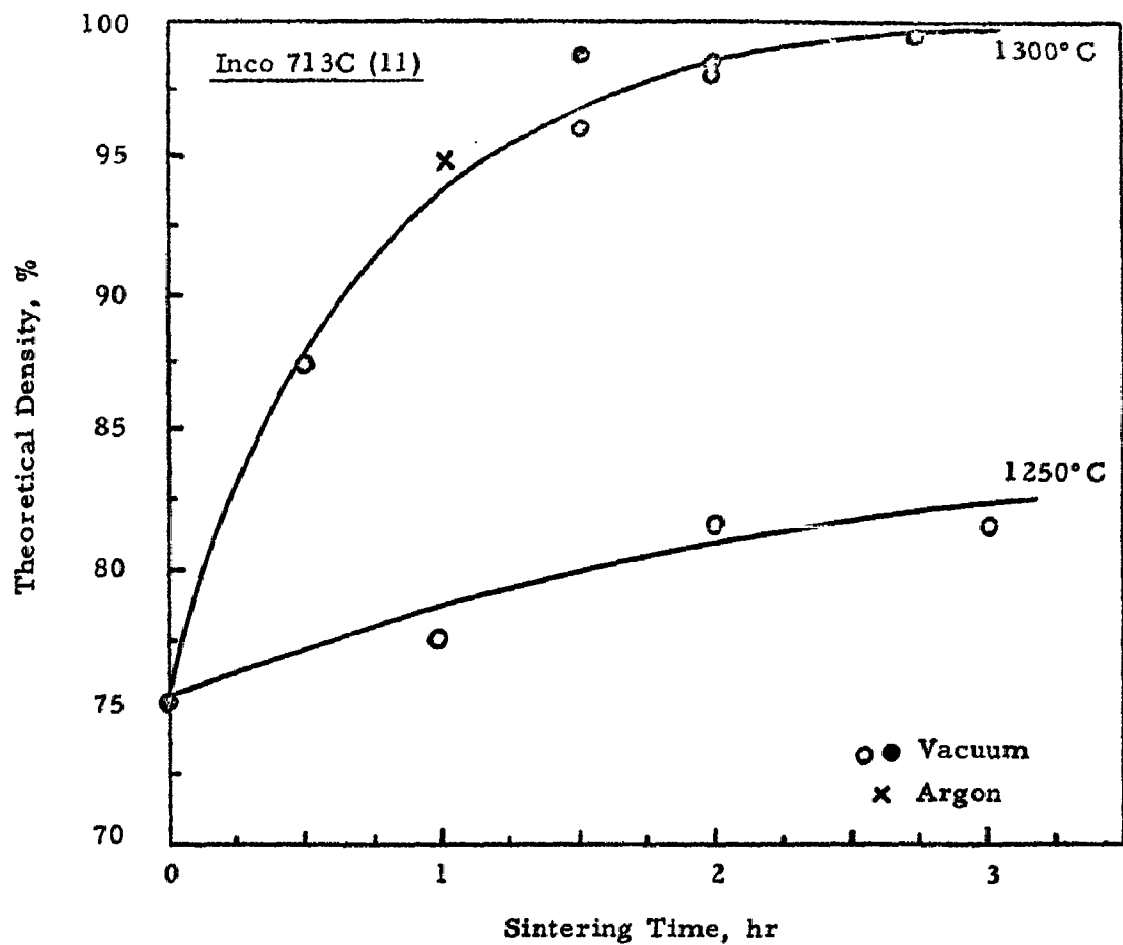


FIG. 7 - Influence of Sintering Time at Several Temperatures on the Density of Inco 713C Powder Compacts

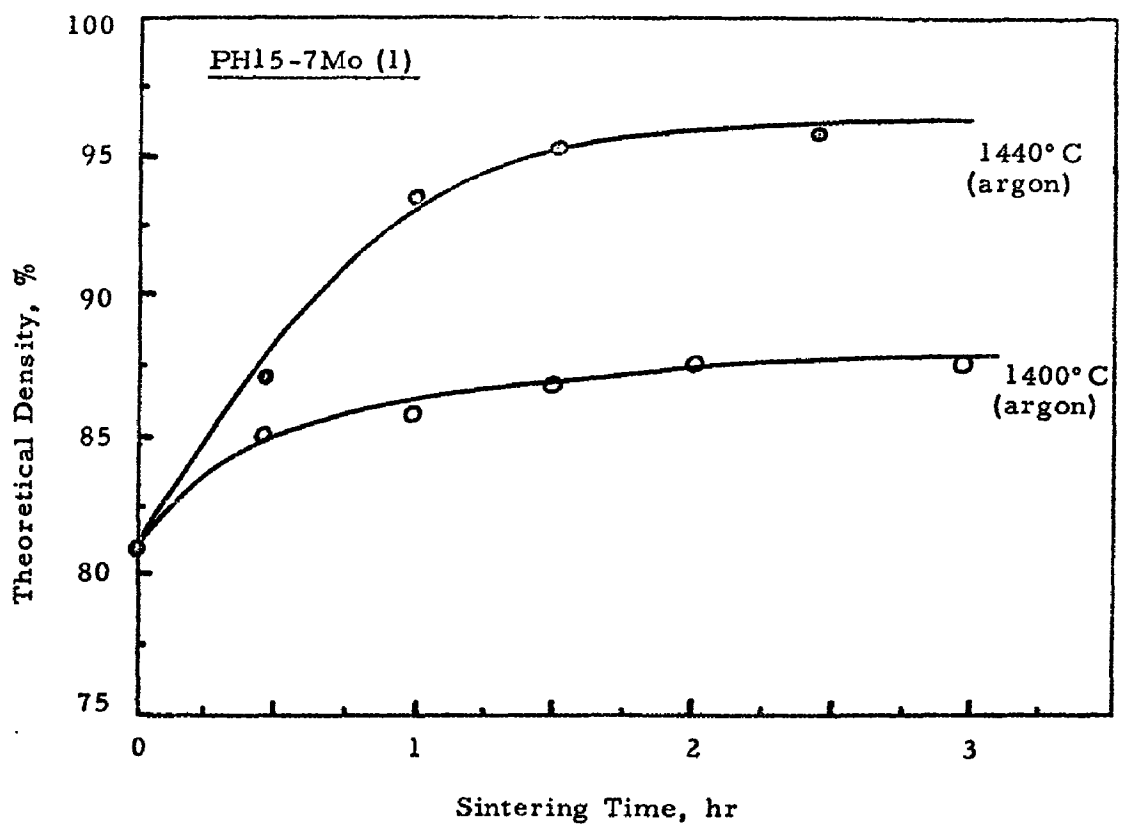


FIG. 8 - Influence of Sintering Time at Several Temperatures on the Density of PH15-7Mo Powder Compacts. Sintering atmosphere--argon.

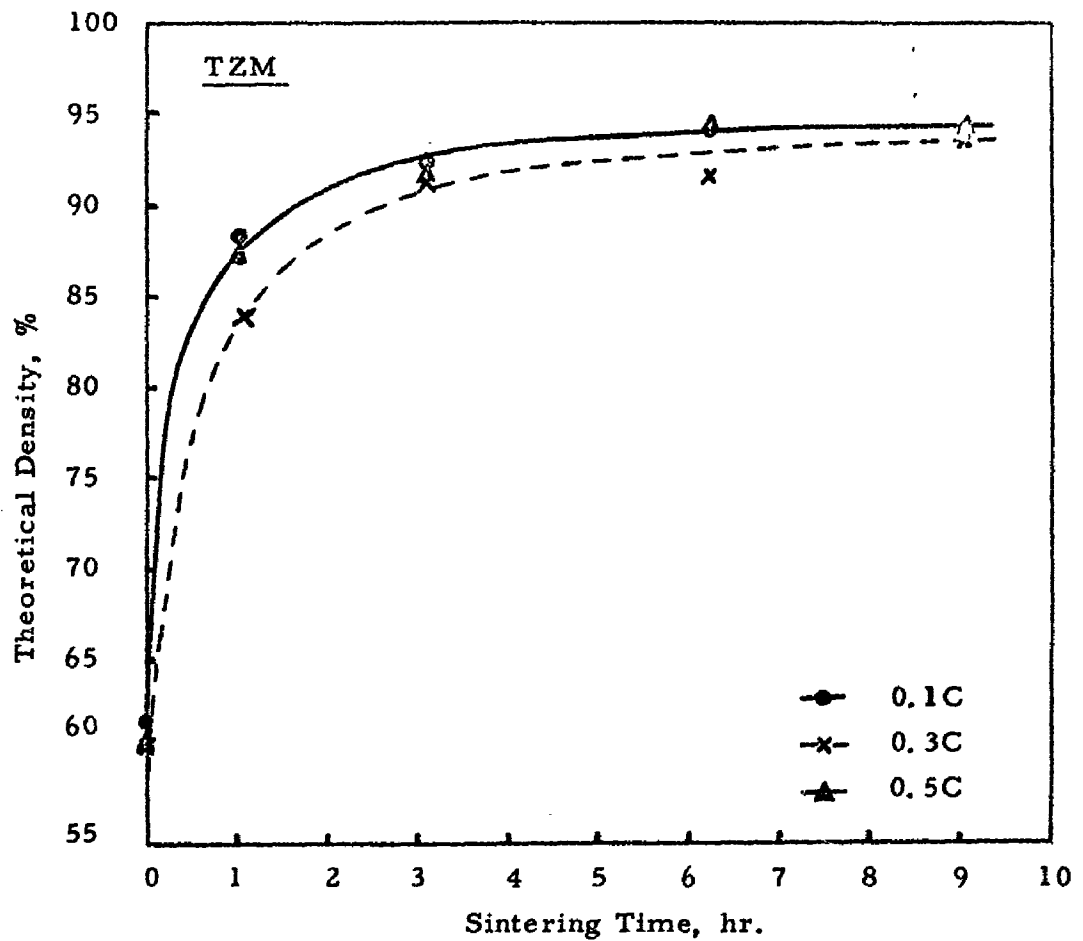


FIG. 9 - Influence of Sintering Time at 2000° C (in vacuum) on the Density of Synthesized TZM Alloys.

For example, the curve for the Udimet 700 alloy in Figure 5 indicates that a 1 hr treatment at 1275°C in a vacuum of 0.1 micron results in a density of 84% of the theoretical value. In Figure 6, a 15 min. treatment at 1275°C gives a theoretical density of 98%. In the former case the specimens were 1 in. dia. cylinders and in the latter, 3/8 in. dia. cylinders. Also, in the latter case, a vacuum of 0.5 micron was attained. Experience shows that when oxygen is present sintering is very slow. If a compact is sintered without first allowing it to degas slowly at some lower temperature, very poor sinters are obtained. This applies in a vacuum or in argon. It is probable that the partial pressure of oxygen over the specimen during sintering has a more pronounced effect on sintering rate than does the sample size. This point will be investigated.

Figure 6 also shows that 1200°C is obviously too low a sintering temperature for Udimet 700 powder; even after 3 hr the density does not exceed about 92% of the theoretical value. An acceptable value for the manufacture of forging or extrusion billets is about 95% or better (for all the atomized alloys). A 1 1/2 hr treatment of Udimet 700 at 1250°C under the experimental conditions of vacuum gives 97% of the theoretical density, with uniform shrinkage. Shorter times at higher temperatures tend to induce "squatting" in the compacts and would thus give distorted billets requiring excessive machining. Similar conclusions are drawn for the Inco 713C and PH15-7Mo alloys (Figures 7 and 8) where the optimum sintering conditions appear to be 1 1/2 hr at 1300°C in vacuo, and 1 1/2 hr at 1440°C in argon, respectively. As mentioned earlier, these conditions also cause no noticeable changes in the chemical compositions of the alloys. On the large compacts (e. g. about 4 in. dia x 7 in. high) required for the extrusion studies the above experimental conditions may have to be varied a little to account for the differences in the size of the compacts, the heavier mass (creep and squatting effects), and the slower heating rates. The present studies, however, provide a close guide around which some subsequent sintering tests on the large billets can be made under the industrial-type sintering conditions.

The synthesized TZM alloys, as pointed out in Section II-B, do not have the expected carbon and oxygen contents but in other respects are of TZM composition. Since this alloy is based on the refractory metal molybdenum, high sintering temperatures are required. The influence of sintering time on the density of TZM compacts held at 2000°C in vacuo is shown in Figure 9. The broken line in Figure 9 is below the other curve because the specimen contained a large crack that did not seal. The maximum density attained was 94% of the theoretical value, and this is thought to be acceptable for forging and extrusion work. However, further tests will be made at higher temperatures to obtain greater densities in shorter times.

D. Metallographic Examination of the Sintered Alloys

1. Udimet 700

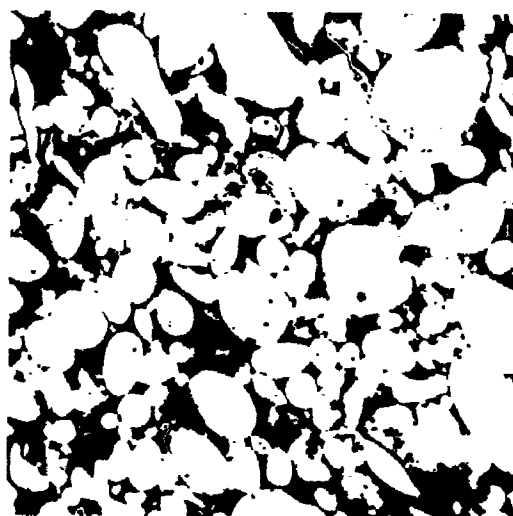
Figure 10 is typical of the very coarse-grained, acicular structure found in the as-received, as-cast Udimet 700 melt stock. The precipitate is possibly one of a  $\text{Co}(\text{Cr})\text{Ni}_3$  phase in a nickel-rich matrix. Many small pores are also evident. The structure of the as-compacted, -80 mesh Udimet 700 powder, with a density of about 75% of the theoretical value, is represented by Figure 11. The particles are rounded and very closely packed. On sintering for 3 hr at 1200°C in vacuum the bulk of the pores close and the microstructure shown in Figure 12 is obtained. Here, the rounded particles have formed twinned, polygonal grains. Some large pores and many fine pores are still obvious, and the theoretical density is now about 92%. The optimum conditions of sintering appear to occur at 1250°C for this alloy. At this temperature the large pores disappear and the theoretical density rises to about 97%. Some grain growth occurs but the grain size is still very much smaller than that in the as-cast material. Figure 13 shows the typical microstructure in this condition. It is not certain what the grain boundary phase is. Further investigation will reveal whether it is an intermetallic compound or an oxide phase.



Neg. No. 24646 X150

Fig. 10

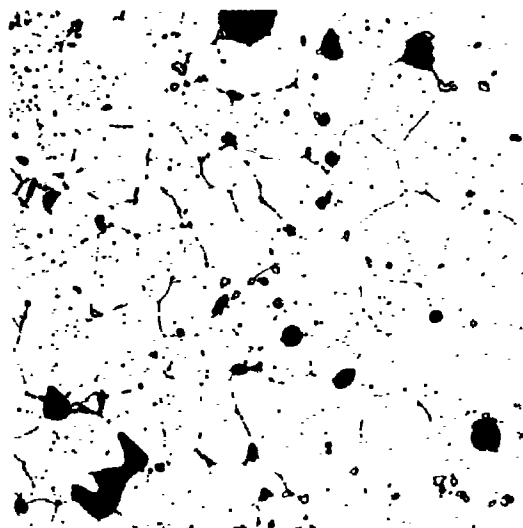
As-received, as-cast Udimet 700 alloy showing very large acicular grains.



Neg. No. 24641 X150

Fig. 11

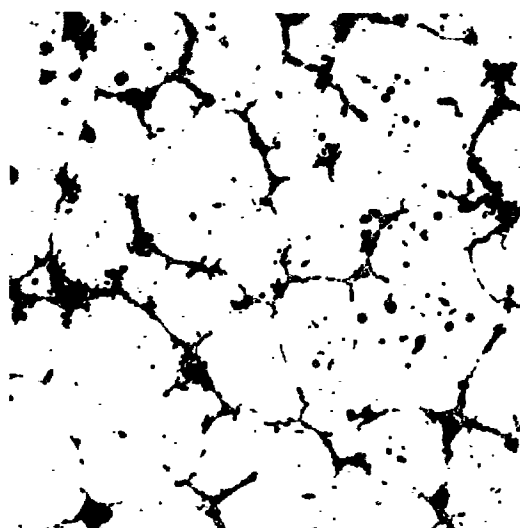
-80 mesh powder of Udimet 700 as-compacted for sintering.



Neg. No. 24700 X150

Fig. 12

Udimet 700 powder sintered 3 hr at 1200°C in vacuum.



Neg. No. 24702 X150

Fig. 13

Udimet 700 alloy fully sintered at 1250°C in vacuum.

## 2. Inco 713C

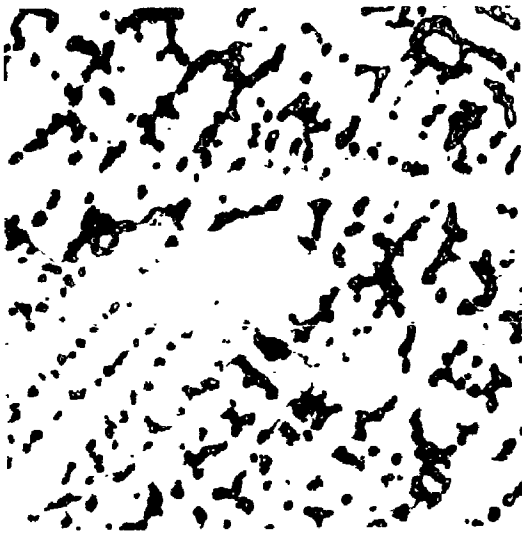
The structure of the as-cast material is illustrated in Figure 14, where an entrapped second phase, probably of molybdenum- or aluminum-base intermetallic compounds, can be seen between large dendrites of nickel-rich solid solution. The atomized powder, on compaction (Figure 15), looks much the same as that of the Udimet alloy. On sintering in vacuum at 1300°C for 30 min, the apparent density increases from 75% to about 87%, and the microstructure then looks like that in Figure 16. Further treatment at 1300°C closes the voids and causes a small increase in grain size (Figure 17). The closure of the voids also results in the formation of a second phase mainly at three-cornered grain junctions from which the voids disappear last. This suggests that the second phase may have been on the surfaces of the voids, in which case, previous discussion intimates that the phase may be an oxide.

## 3. PH15-7Mo

The microstructure of the as-cast PH15-7Mo alloy (Figure 18) is very similar to that of the as-cast Udimet 700 alloy but in this case is probably composed of a precipitate of austenite in a solid solution of nickel and chromium in bcc iron. PH15-7Mo powder sinters readily in argon; a 30 min treatment at 1440°C gives a theoretical density of about 87% and the microstructure shown in Figure 19. The coarse martensitic structure is retained after sintering and is even more obvious in a specimen sintered at 1440°C to a density of 95% of the theoretical value, in Figure 20, where the last of the pores has almost disappeared and no grain boundary phases can be seen.

## 4. TZM Alloy

As mentioned in Section C the synthesized TZM alloys do not meet the chemical specification because of their low carbon contents and high oxygen contents. Moreover, despite their initial carbon contents, after sintering the three alloys can be regarded as one. However, the sintering behavior displayed by the alloys should be very much the same

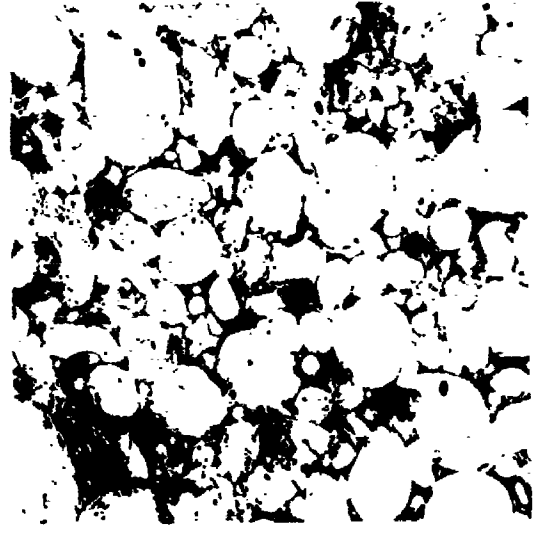


Neg. No. 24703

X150

Fig. 14

As-received, as-cast Inco 713C alloy showing coarse dendritic structure.

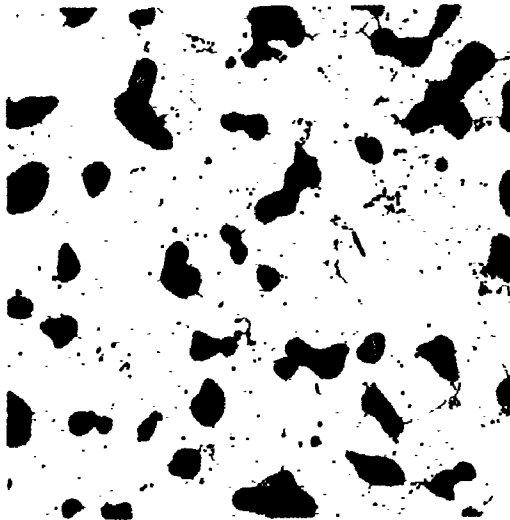


Neg. No. 24636

X150

Fig. 15

-80 mesh powder of Inco 713C compacted for sintering.

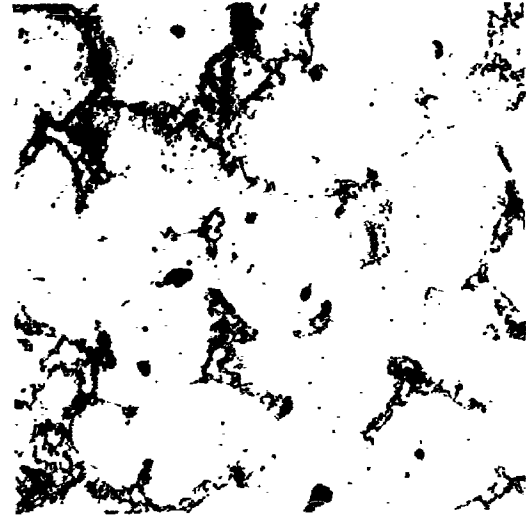


Neg. No. 24639

X150

Fig. 16

Inco 713C powder sintered for 30 min at 1300°C in vacuum.

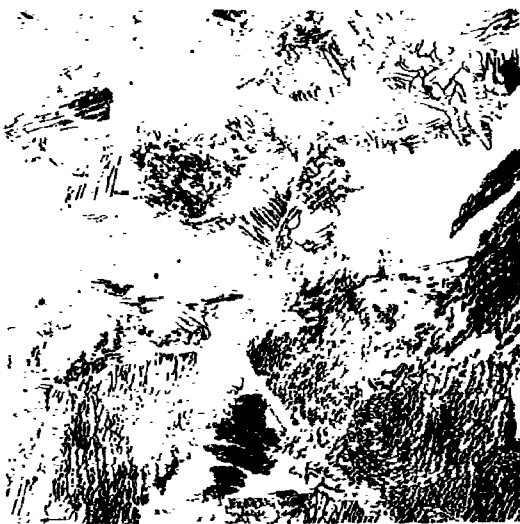


Neg. No. 24640

X150

Fig. 17

Inco 713C alloy fully sintered at 1300°C in vacuum.

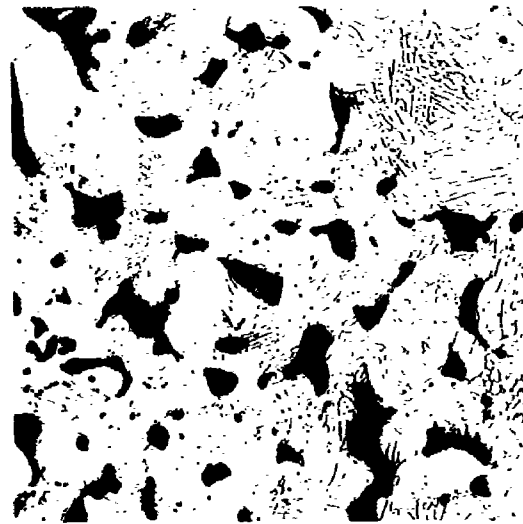


Neg. No. 24649

X150

Fig. 18

As-received, as-cast PH15-7Mo alloy showing coarse martensitic-type structure.



Neg. No. 24638

X150

Fig. 19

PH15-7Mo powder sintered for 30 min at 1440°C in argon.

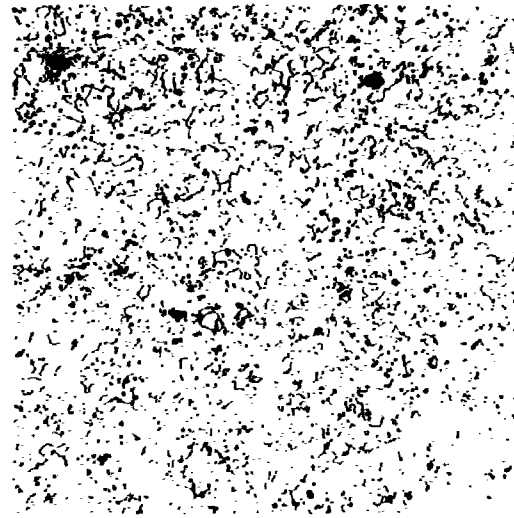


Neg. No. 24712

X150

Fig. 20

PH15-7Mo alloy sintered 1 hr at 1440°C in argon.



Neg. No. 24652

X250

Fig. 21

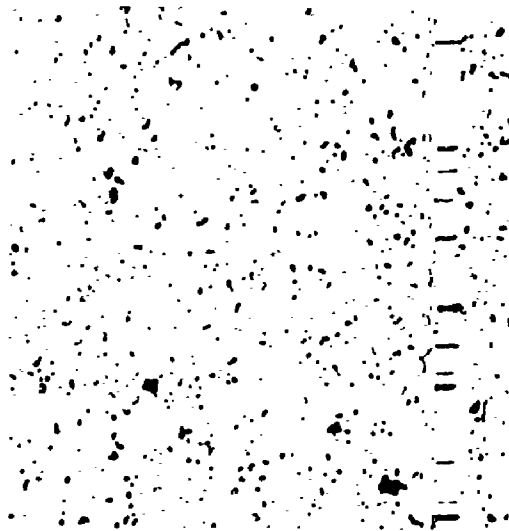
Synthesized TZM alloy sintered 1 hr at 2000°C in vacuum.

as that of a true TZM alloy. Figure 21 shows the nominal 0.1%C alloy after sintering for 1 hr at 2000°C in vacuum. The 0.3 and 0.5%C alloys also look exactly like Figure 21. The grain size is very small and equiaxed, and little porosity can be seen even though the density at this stage is only about 87% of the theoretical value. On further heating, the grain size grows quite markedly with sintering times up to 6 hr (Figure 22), above which grain growth is retarded (Figure 23). Long sintering times appear to cause the formation of larger voids as well as larger grains without change in density. It is possible that this growth may be related to the high oxygen content of the metal. Another observation on the material that has been sintered for long times (Figures 23) is the appearance of fairly large particles of a second phase. These appear to have no connection with voids.

### III. CONCLUSIONS AND FUTURE WORK

The object of the work to date has been to determine the conditions for the production and sintering of superalloy powders. The powders produced by atomization have shown themselves to be suitable for processing to sintered billets. During processing they suffer little change in over-all chemical composition but may gain a little in oxygen content, which might cause subsequent difficulties; this problem is receiving further consideration.

The boundary conditions for sintering of the superalloy powders have been fairly well settled, and the feasibility of synthesizing TZM alloy has been established. So far the purity of the starting materials used in the work has not been too high. It is expected that in the high-purity metals to be used in the production of the forgings and extrusions, the formation of the second phases noted in Section II-D will not occur. The material being processed now has a total gas content of about 60 ppm.

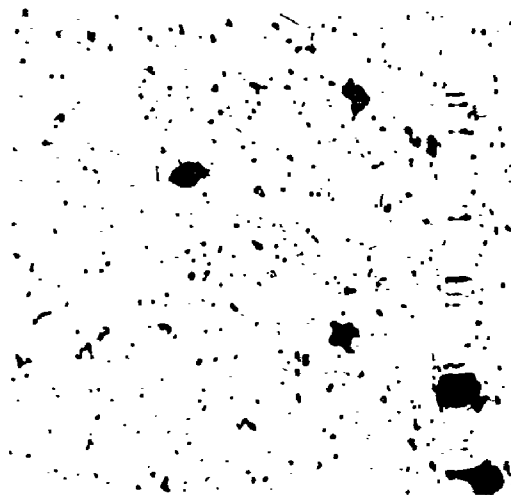


Neg. No. 24653

X250

Fig. 22

Synthesized TZM alloy sintered 6 hr  
at 2000° C in vacuum.



Neg. No. 24711

X250

Fig. 23

Synthesized TZM alloy sintered 9 hr  
at 2000° C in vacuum.

Future work will be concerned with overcoming the problems noted in this report and with the production of suitable forgings and extrusions in accordance with the terms of Phase II of the subject contract.

Respectfully submitted,

ARMOUR RESEARCH FOUNDATION OF  
ILLINOIS INSTITUTE OF TECHNOLOGY

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