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LOS ALAMOS SCIENTIFIC LABORATORY
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LOS ALAMOS • NEW MEXICO

Characterization of
Commercial Refractory Metal
and Metal Carbide Powders

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by

**R. E. Riley
J. E. Magnuson**

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CHARACTERIZATION OF COMMERCIAL REFRACTORY

METAL AND METAL CARBIDE POWDERS

by

R. E. Riley
J. E. Magnuson

ABSTRACT

Practical application of various mixing theories and powder characterization data has been extremely limited over the years. The problems associated with development of a suitable powder procurement specification have complicated matters still further.

Recent developments at Los Alamos Scientific Laboratory (LASL) show that a variety of morphological types of structure are obtainable as a result of the manufacturing processes employed and that more than one type of structure can result from the same manufacturing process. Four basic morphological types of structures have been identified for the powders examined to date, and their influence on final properties have been evaluated. It is felt that the development work described in this paper constitutes a breakthrough for better understanding of the practical application of powder characterization data. Significant to this work is the fact that, with the aid of morphology, one can indeed develop a procurement specification for a powder to meet a particular requirement.

INTRODUCTION

The physical limitations of the more common materials at very high temperatures have led to exploration of a class of materials which might possess some useful characteristics under these extreme conditions. About two years ago the Materials Technology Group at Los Alamos Scientific Laboratory (LASL) was requested to evaluate such a product. The materials in question were hot-pressed composites of carbide and graphite.

A program was established to systematically investigate the many parameters related to fabrication of a composite material and to correlate these variables with properties of the composites. Two types of graphite and the refractory carbide powders of Nb and Ta were included in the investigation. The

need for full characterization of the powders was recognized early in the program.

At first, a single lot of powder, TaC-13A, was used. Weighed quantities of the carbide powder were blended with various quantities of graphite, loaded into graphite dies, and hot-pressed at temperatures of about 3000°C and pressures ranging from 2000 to 5000 psi. This powder had a Fisher average particle size, or Fisher sub-sieve (FSS) size, of 2.0 μ , and approximately 50% of its particles were less than 2.0 μ in diameter. It was learned that the fines had a tendency to agglomerate during blending. Upon hot-pressing, the agglomerated particles produced a non-uniform distribution of very large carbide platelets oriented perpendicular to the direction of pressing. This resulted in highly directional properties in

the as-pressed product.

A second lot of powder, NbC-9, was selected for the work that immediately followed. The problem of aggregate and subsequent platelet formation was not observed in pressings made from this powder.

As the program expanded, it became necessary to procure more powders. Sample lots NbC-10A through 10E were received from five different vendors in accordance with the following procurement specification: NbC powder, -325 mesh, highest purity available, nominal FSS size of 2.0 to 2.5 μ . Information upon which to base a more detailed specification was not available at that time. Preliminary results from high temperature creep tests on specimens fabricated from these powders indicated wide scatter and numerous anomalies in the data.

The distribution curves of these vendor evaluation lots varied significantly from that of lot NbC-9, as shown in Fig. 1. This difference was also reflected in the metallographic structure of the samples shown in Fig. 2.

Fig. 1. Particle size distribution curves of selective NbC evaluation powder lots.

It was decided to procure additional powders from vendor "E" for comparison with other lots of powders previously supplied by the vendor. Figure 3 shows the variations observed in six additional lots of powder obtained from vendor "E". Differences occurred not only in the physical characteristics but also in the chemistry, even though all of the powder lots were represented by the vendor as being similar and made by the same manufacturing process.

At this point in the program, a critical review of all refractory carbide powders on hand was initiated. The graphite component was well characterized, and the same material was used in the preparation of all composites.

It is the authors' intent to demonstrate that full characterization of a powder, including its shape and structure, enables one to be more scientific in the design of reproducible, economic powder metallurgy fabrication process. It will be shown that with this information on the powders, plus a limited fabrication development program, a procurement specification for powder can be determined which can help realize a more reproducible fabrication process.

DISCUSSION

Commercial Carbide Powders

The powders analyzed for this part of the investigation represented 42 lots of NbC, 14 lots of TaC, and 6 lots of ZrC, all obtained from various vendors; the evaluation, summarized in this section, was the subject of a previous report.¹ The characterization data obtained for the various powder lots are summarized in Table I.

An attempt was made at IASL to provide a basis for identification of the morphological types observed in commercial, as-received powders. This phase of the investigation involved only those types of structures and shapes associated with the manufacturing techniques used to make the powder. It did not involve the morphological type generally associated with second phases, oxide films, and vestiges of segregate.

The various types of structures resulting from the same or different techniques used to manufacture commercial powders may have a profound effect on the mechanical and physical properties of a fabricated part. The powders evaluated in this study were examined for the following: (1) density -- particles

Fig. 2. Microstructure of NbC powders from various vendor evaluation lots. 250X.

Fig. 3. Microstructure of various lots of NbC powder from a single vendor. 250X.

TABLE I
NbC POWDER CHARACTERIZATION DATA

Powder Lot No.	Density g/cc		Average Particle Size, μ	Specific Surface		Morphological Type
	Bulk	Tap		BET	Fisher	
ZrC-4	2.33	3.17	2.97	1.06	0.31	B
ZrC-5	1.98	2.78	5.4	0.84	0.17	C
ZrC-6	2.00	2.84	2.70	1.08	0.34	B
ZrC-7	2.05	3.13	2.75	1.19	0.33	C
ZrC-8	2.26	3.47	3.00	1.30	0.30	B
ZrC-9	2.41	3.70	5.27	0.734	0.17	B
TaC-6	4.83	6.61	5.40	0.29	0.77	B
TaC-7	5.51	7.32	10.20	0.60	0.04	B
TaC-8	4.69	6.70	2.18	0.75	0.19	B
TaC-9	5.13	7.44	2.10	1.01	0.20	B
TaC-10	5.26	7.47	2.10	0.89	0.20	B
TaC-11	5.19	7.33	2.25	0.89	0.18	B
TaC-12	2.88	3.36	7.00	0.825	0.06	C
TaC-13A	4.70	6.91	2.00	0.82	0.38	B
TaC-13B	4.98	6.21	1.35	1.26	0.31	B
TaC-13C	4.88	6.09	1.70	0.997	0.24	B
TaC-16	8.73	9.48	50.0	-	0.008	B
TaC-17	7.50	8.34	38.4	0.137	0.11	B
TaC-18	4.97	7.69	2.55	0.637	0.162	-
TaC-19	5.05	8.42	2.45	0.772	0.167	B
NbC-6	2.09	3.27	1.30	2.58	0.59	B
NbC-7	1.48	3.98	1.94	1.24	0.33	D
NbC-9	2.21	3.98	3.90	1.28	0.20	B
NbC-10A	2.72	3.77	3.60	1.12	0.21	B
NbC-10B	2.51	3.62	3.65	0.81	0.21	B
NbC-10C	2.53	3.77	3.87	0.84	0.20	B
NbC-10D	2.36	3.72	2.00	1.78	0.38	B & C
NbC-10E	2.36	3.72	3.48	1.43	0.22	B
NbC-11	2.38	3.38	3.00	0.88	0.26	B & D
NbC-12	2.62	3.90	2.80	1.22	0.27	B
NbC-13	2.90	4.24	3.60	0.92	0.21	B
NbC-13R	3.02	4.25	4.02	0.885	0.191	B
NbC-14	3.22	4.14	12.7	0.28	0.06	A
NbC-15	2.57	3.93	3.5	0.97	0.22	B
NbC-17	2.89	4.18	3.5	1.03	0.38	B
NbC-17A	2.65	4.14	3.65	0.87	0.21	B
NbC-17AR	3.13	4.26	4.11	0.788	0.187	B
NbC-18A	2.73	4.46	3.8	0.94	0.202	-
NbC-19	5.05	8.42	2.45	0.854	0.210	B
NbC-20	3.13	4.65	4.79	0.587	0.161	B
NbC-21A	1.56	2.44	1.30	2.160	0.590	B
NbC-21B	1.74	2.56	1.29	2.169	0.595	B
NbC-21C	1.60	2.35	1.29	1.224	0.595	B
NbC-22A	2.80	4.23	3.55	0.714	0.219	B
NbC-22B	2.69	4.31	3.90	0.813	0.197	B
NbC-22C	2.67	4.40	3.85	0.743	0.199	B
NbC-23A	3.00	4.46	3.91	0.714	0.196	B
NbC-23B	2.96	4.31	4.05	0.824	0.189	B
NbC-23C	2.98	4.35	4.05	0.843	0.189	B
NbC-23AA	2.88	4.38	3.55	-	0.216	B
NbC-23BB	3.11	4.28	4.0	0.864	0.192	B
NbC-23CC-1	3.20	4.56	4.25	-	0.181	B
NbC-23CC-2	2.71	4.20	3.62	-	0.209	B
NbC-23CC-3	2.89	4.30	3.60	-	-	-
NbC-24	2.82	4.32	3.01	1.072	0.255	-
NbC-25	2.97	4.74	4.50	0.622	0.171	-
NbC-26	2.71	4.27	3.35	-	-	B
NbC-27	2.87	4.49	4.20	-	0.183	B
NbC-28A	2.84	4.21	3.47	-	0.221	B
NbC-28B	2.61	3.99	3.42	-	0.224	B
NbC-28C	2.59	4.11	3.38	-	0.227	B
NbC-29	2.59	4.08	3.11	-	-	B

are either solid or porous, (2) structure -- a discrete particle or an agglomerate of fines, and (3) size and shape of the particle. Four basic morphological types of structure have been identified for the powders examined to date.

The first morphological type, Type A (Fig. 4), is a porous particle which is apparently the result of the manufacturing technique employed. The menstrum process, in which the particle is formed in a molten metal bath, was used in making this powder. This type of particle is quite strong and is a discrete particle. Upon hot-pressing such a product with graphite, this large porous particle collapsed to a flat platelet, resulting in anisotropy in the finished product.

This powder, Lot NbC-14, had a FSS size of 12.7μ , which was much coarser than most of the powders investigated. It is not known whether size had any bearing on the porosity, because another lot of powder, NbC-10B, of much lower FSS size but manufactured by the same technique, yielded a very dense particle of extremely uniform size.

The most common morphological type observed in powders is Type B (Fig. 5), which may be described as a dense particle of either rounded or angular shape. This type of particle was most desirable for making hot-pressed carbide-graphite composites. The Type B particle contributed significantly to reducing anisotropy; however, it did not completely eliminate it. The graphite used in this work is believed to be responsible for the anisotropy which, while present, was not excessive.

Type C, shown in Fig. 6, is similar to Type A in that both are porous. However Type C differs from Type A in that the structure of Type C is an aggregate of a large amount of very fine particles. Also, the Type C structure partially breaks up on ball milling, whereas the Type A structure is far more resistant to fracture. The Type C particle mixed with graphite also flattens during hot-pressing, giving rise to considerable anisotropy in the product.

A fourth type of structure observed was designated Type D (Fig. 7). Discussions with technical representatives of two vendors supplying such a product indicated that the carbothermic reduction process yielded a variety of structures. They indicated that the Type D structure, a hollow-like

particle, was a result of incomplete reaction even though the material might be stoichiometric. The structure can be altered by further thermal processing.

On further evaluation of the powders the characterization data, including metallographic examination, enabled a revised procurement specification to be written, based on the observation that powders of a particular FSS size, having a minimum bulk and tap density, would have the same structure. This revised specification for NbC powder follows:

-325 mesh NbC powder -- highest purity available, nominal FSS size of 3.5 to 4.0μ . The material must have a minimum bulk density of 2.7 g/cc and a minimum tap density of 4.25 g/cc.

Powders purchased to this specification had the desired Type B structure when parameters were met. It was necessary to add a chemistry specification at a later date because of metallic impurities apparently picked up during the comminution process. The effects of these impurities are discussed in another paper¹ and will not be discussed further in this report other than to emphasize that purity is always a significant characteristic of a powder.

The results of the study of powder shape and structures were of tremendous help in understanding the various characterization data obtained on the powders. The scatter in the powder characterization data was resolved when the shape and structure of the powders involved were correlated to other properties. In fact, similar specifications written for ZrC and TaC yielded most satisfactory results in obtaining powders of the desired morphology (Type B) essential to our program on composites.

Of the carbide powders evaluated to date, only one lot was Type A; three were Type C, two were Type D, and the balance were Type B. Based on these data, an attempt was made to correlate the various parameters of the characterization data. Because of the insufficient number of data points, this attempt was limited to the Type B product.

A plot of bulk and tap density vs FSS size for the NbC powders of differing morphology is presented in Fig. 8. A scatter band is drawn to show the range of values obtained for the Type B powders. The breadth of the band is controlled by the particle size distribution and the variability of porosity within the powders.

Fig. 4. Type A. ~ 1000X.

Fig. 5. Type B. 1000X.

Fig. 6. Type C. 1000X.

Fig. 7. Type D. 1000X.

Fig. 8. Bulk and tap density vs FSS size for all NbC powder lots.

Figure 9 is a plot of specific surface area, as determined by the Brunauer, Emmet, Teller (BET) method, as a function of FSS size. If one draws a scatter band for the Type B powders, a correlation exists. Again, a careful study of the data revealed that the breadth of this band is controlled by the particle size distribution and the porosity within the powders. This is best demonstrated by comparing the BET measurements and microstructures of powder lots NbC-10B and NbC-10C, which had FSS sizes of 3.60μ and 3.65μ , respectively. The distribution curves (Fig. 1) of these two powders are quite different, and the microstructure of NbC-10B (Fig. 2) is more porous than that shown for lot NbC-10C. The data points for the other morphological types are included on these graphs. Unfortunately, there are not enough data points to draw similar curves for each type.

Molybdenum Powder

Concurrent with the work on carbide powders was a similar program on Mo powders. Nineteen lots of

Fig. 9. Specific surface area vs FSS size for all NbC powder lots.

Mo powder having a wide range of particle size were fully characterized. The data are presented in Table II. All powders were purchased at the highest purity available. Fifteen powder lots had a Type B structure; two of these lots, Mo-3 and Mo-17, were doped with 1 wt. % ThO_2 during manufacture. The remaining four lots were of Type C morphology.

Figure 10 shows the correlation which exists between bulk and tap density as a function of FSS size. You will note that there is less scatter in the data on the Mo powders of the Type B structure than was observed for the NbC powders (Fig. 8). This is because the Mo powders had little or no porosity, whereas the NbC powders, although classed as Type B, showed varying degrees of porosity. The spread in the data for the Mo powders having a Type B structure is therefore attributed primarily to the differences in particle size distribution.

Although only four lots of powder were of Type C structure it is felt that these data points, shown in Fig. 10, demonstrate that morphology plays a very important role in understanding and applying the

TABLE II
CHARACTERIZATION AND COMPRESSIBILITY AND SINTERING DATA
FOR SELECTIVE MOLYBDENUM POWDERS

	Mo-36	Mo-10	Mo-25	Mo-26	Mo-12	Mo-19	Mo-20	Mo-13	Mo-8	Mo-37
FSS- μ	2.31	3.45	4.00	4.00	4.30	4.30	4.60	4.60	4.80	5.00
Bulk ρ	1.33	1.86	1.15	1.11	1.87	1.57	1.39	1.77	2.28	2.95
Tap ρ	2.04	2.93	2.75	2.75	3.31	2.39	2.57	3.23	3.96	4.34
S _w -BET	1.364	-	1.095	1.022	0.772	0.532	-	0.652	-	0.483
S _w -F	0.255	0.179	0.154	0.156	0.137	0.135	0.137	0.138	0.123	0.118
Morphology	"B"	"B"	"B"	"B"	"B"	"B"	"B"	"B"	"B"	"B"
10,000 psi Compaction Pressure										
ΔL	24.00	19.20	19.21	19.57	19.52	20.44	20.28	18.84	16.73	17.19
ΔD	26.10	21.22	19.51	20.00	20.98	20.73	20.49	20.73	18.54	18.78
ρ_0	4.06	5.00	4.99	4.94	4.92	4.82	4.80	4.97	5.36	5.37
ρ_1	9.30	9.66	9.05	9.11	9.09	8.65	8.78	9.08	8.92	8.30
ρ_2	9.55	9.77	9.33	9.43	9.62	9.44	9.43	9.61	9.59	9.45
20,000 psi Compaction Pressure										
ΔL	20.47	16.18	15.18	16.58	15.79	14.84	16.47	15.29	14.04	11.32
ΔD	22.68	19.02	15.83	17.56	18.05	17.07	17.07	17.56	16.34	16.59
ρ_0	4.74	5.50	5.63	5.51	5.55	5.45	5.49	5.66	5.89	5.81
ρ_1	9.55	9.69	9.37	9.42	9.32	9.08	9.19	9.33	9.20	8.69
ρ_2	9.77	9.87	9.58	9.58	9.72	9.42	9.46	9.72	9.68	9.58
40,000 psi Compaction Pressure										
ΔL	16.67	12.68	11.86	12.27	11.56	12.74	12.15	11.37	11.17	11.39
ΔD	18.05	15.61	13.17	14.15	14.63	13.56	12.93	13.90	13.20	13.90
ρ_0	5.65	6.27	5.51	6.31	6.35	6.33	6.49	6.51	6.66	6.54
ρ_1	9.60	9.79	9.64	9.62	9.44	9.35	9.53	9.43	9.41	9.02
ρ_2	9.88	9.94	9.57	9.63	9.77	9.56	9.59	9.76	9.79	9.62
80,000 psi Compaction Pressure										
ΔL	11.97	9.20	7.74	7.91	8.38	8.21	8.15	7.22	7.30	8.42
ΔD	12.93	10.73	8.05	9.02	9.76	8.54	8.29	9.27	9.02	9.76
ρ_0	6.73	7.24	7.54	7.43	7.47	7.46	7.52	7.58	7.67	7.53
ρ_1	9.72	9.64	9.61	9.56	9.47	9.38	9.53	9.50	9.49	9.36
ρ_2	9.95	9.87	9.41	9.56	9.80	9.61	9.54	9.82	9.86	9.76

TABLE II (Continued)
CHARACTERIZATION AND COMPRESSIBILITY AND SINTERING DATA
FOR SELECTIVE MOLYBDENUM POWDERS

	Mo-38	Mo-35	Mo-18	Mo-7	Mo-28	Mo-31	Mo-30	Mo-17 ^a	Mo-3 ^a
FSS-μ	5.04	5.17	5.90	2.88	6.20	6.80	7.40	4.15	6.70
Bulk ρ	2.73	3.08	2.24	1.94	1.66	1.67	1.63	2.00	2.92
Tap ρ	4.08	4.25	3.31	2.35	2.10	2.11	1.99	3.46	4.56
S _w -BET	0.386	0.278	0.384	0.848	1.393	1.494	2.471	0.792	0.630
S _w -F	0.117	0.114	0.103	0.204	0.089	0.087	0.079	0.142	-
Morphology	"B"	"B"	"B"	"C"	"C"	"C"	"C"	"B"	"B"
10,000 psi Compaction Pressure									
ΔL	16.54	16.97	12.09	24.24	27.36	26.24	25.26	18.34	6.32
ΔD	18.29	18.54	13.41	24.88	26.59	27.56	26.83	19.76	8.05
ρ ₀	5.46	5.33	5.48	4.02	3.51	3.45	3.58	5.02	5.54
ρ ₁	8.96	9.06	6.65	8.56	8.31	7.99	8.22	7.92	5.74
ρ ₂	9.61	9.50	8.14	9.19	8.67	8.72	8.75	9.40	6.86
20,000 psi Compaction Pressure									
ΔL	13.69	13.60	9.84	21.79	22.75	22.83	23.20	14.77	5.20
ΔD	16.59	16.34	12.20	22.69	22.93	23.66	23.90	17.07	6.34
ρ ₀	5.89	5.93	6.10	4.54	4.30	4.27	4.22	5.61	6.04
ρ ₁	9.03	9.13	7.31	8.92	8.89	8.80	8.76	8.59	6.25
ρ ₂	9.56	9.65	8.63	9.37	9.20	9.25	9.21	9.39	7.27
40,000 psi Compaction Pressure									
ΔL	10.91	10.31	8.19	18.01	18.56	19.02	19.12	9.66	2.98
ΔD	13.66	13.41	10.00	19.02	19.27	19.02	19.27	11.95	4.39
ρ ₀	6.56	6.61	6.86	5.33	5.18	5.19	5.17	6.37	6.82
ρ ₁	9.32	9.34	8.00	9.35	9.17	9.25	9.30	9.10	7.02
ρ ₂	9.77	9.69	9.02	9.64	9.48	9.56	9.52	8.94	7.59
80,000 psi Compaction Pressure									
ΔL	7.49	8.00	5.77	13.74	14.01	16.23	14.20	7.87	2.93
ΔD	9.51	9.02	6.59	13.90	14.39	14.15	14.39	8.78	2.68
ρ ₀	7.52	7.50	7.81	6.41	6.31	6.18	6.35	7.42	7.81
ρ ₁	9.37	9.32	8.68	9.64	9.55	9.52	9.58	9.50	7.98
ρ ₂	9.72	9.69	9.33	9.75	9.77	9.73	9.77	9.48	8.37

^a 1 wt % ThO₂ doped.

Fig. 10. Bulk and tap density vs FSS size for Mo powder lots having Types B and C morphology.

characterization data. For example, the bulk and tap density increase with increasing particle size for the Type B powder. On the other hand, these parameters appear to be unaffected by particle size for the particle size range (~ 2 to 7.5μ) investigated.

The correlation between FSS size and specific surface determined by the BET method and from the Fisher data is shown in Fig. 11. The specific surface decreases with increasing particle size for the Type B powders as determined by the BET method. On the other hand, the specific surface of the Type C powders increases with increasing average particle size. This relationship is consistent with the quantities being determined.

The value for specific surface obtained from the Fisher data is dependent upon the average particle size of the powder and gives an estimate of

Fig. 11. Specific surface area vs FSS size for Mo powder lots having Types B and C morphology.

smooth envelope surface for each particle. The BET adsorption method actually measures the total exposed area, including all cracks and fissures that are open to the surface. Therefore, the BET data are more accurate and very much structure dependent; the Fisher data do not reflect the influence of morphology.

Powder samples were prepared by compaction in a 0.4-in.-diam hardened steel die at pressures of 10,000, 20,000, 40,000, and 80,000 psi. Double action pressure was applied. All samples were prepared in triplicate with nominal length of the pressed sample being 0.250 in.

All these specimens were sintered identically: i.e., presintering at 1000°C for 15 h in purified hydrogen, intermediate sintering at 1700°C for 3 h in purified hydrogen, and final sintering at 2350°C for 1.5 h in purified argon. Density measurements were made in the green state and after the intermediate and final sintering steps by weight-volume measurements; linear and diametral shrinkages were

determined. These measurements are included in Table II.

Green Densities

Figure 12 indicates that for the Type B structure there is an increase in green density (ρ_0) with increasing compaction pressure from 10,000 to 80,000 psi, varying with the average particle size. Four powder lots, Mo-36, Mo-10, Mo-12, and Mo-18, were selected to show the effect of average particle size over the range 2.31 to 5.9 μ . As the data and curves show, the green density increases with increasing FSS size. The finer powder, 2.31 μ , had the lowest green density, because of the increased friction due to higher surface area.

The green density curves of the Type C structure were unaffected by the FSS size, and all four lots of powder yield curves nearly identical to that obtained for the 2.31 μ powder of the Type B structure. This suggests that, regardless of compaction pressure, the aggregate-type particle collapsed on pressing and behaved like the fines that make up the particles.

Intermediate Sintering Results

As stated previously, the green compacts were sintered at 1000°C for 15 h in purified hydrogen to clean up the surface of the particles. They were then given an intermediate sinter at 1700°C for 3 h in purified hydrogen. The results of this intermediate sinter on density (ρ_1) are presented in Table II for all of the powders investigated. Figure 13 shows the effect of FSS size and compaction pressure on the intermediate sinter density of the Type B powders. Although the three powder lots ranging from 2.31 to 4.3 μ FSS size realized very little increase in density as a function of increasing compaction pressure, each achieved a relatively high sintered density independent of pressing pressure. On the other hand, the 5.9 μ powder showed a definite increase in density with increased compaction pressure; the maximum density, however, after the intermediate sinter was about 87% of theoretical density, as compared with a range of 90 to 95% of theoretical density for the other three powders for all compaction pressures.

The intermediate sinter density curves for the Type C structure were nearly identical to that for the 4.3 μ powder shown for the Type B structure and were not affected by the FSS size of the as-received

powder.

Final Sintering Results

Final sintering was done at 2350°C for 1.5 h in purified argon. The sintered densities (ρ_2) are presented in Table II. Figure 14 shows the effect of particle size and compaction pressure on the final sintered density of the Type B structure. Again the spread in the data is very slight for the three powders which ranged from 2.31 to 4.3 μ FSS size, with the highest density being for the 2.31 μ powder. The effect of compaction pressure had little effect on the final sintered densities of these three powders and ranged from about 93 to 97.5% of theoretical density. The 5.9 μ powder followed the trend indicated in the intermediate sinter. It showed an increase from 80% of theoretical density for the 10,000-psi compaction load to a maximum of 91.5% of theoretical density for the 80,000-psi compaction load. The Type C structure again sintered similar to the 4.3 μ Type B material; however, there appeared to be more scatter in the individual specimen measurements than encountered for the Type B structure.

Effect of Additives

Thoria has been used for many years as a grain growth inhibitor to powder metallurgy products. Two powder lots, Mo-3 and Mo-17, were procured as doped powders containing 1.0 wt % ThO₂. The effect of thoria on the green and sintered density is shown in Figs. 15 through 17. As one would expect, there was practically no difference between the green density of the doped powders and that of the undoped powders of near the same FSS size. The reason for the higher green density of the doped powder at a compaction load of 40,000 psi is not known, but is believed to be due to the breaking up of some of the particles during compaction.

In general, the ThO₂ doped powders did not sinter as well as the undoped powders for any compaction pressure after the intermediate sinter (Fig. 16), with the exception of the nominal 4 μ powder. When compacted at 80,000 psi, this powder sintered to a density nearly that obtained for the undoped powder. Figure 17 shows the density curves for these four powders after the final sintering treatment. The spread between the curves of the 5.9 μ , no ThO₂ powder and the 6.7 μ , 1% ThO₂ powder is greater than was noted after the intermediate sinter. The two nominal 4 μ powders behaved somewhat differently in that there

Fig. 12. Effect of particle size of Type B structure on green density.

Fig. 13. Effect of particle size of Type B structure on 1700°C - 3 h - H_2 sinter density.

Fig. 14. Effect of particle size of Type B structure on 1700°C - 3 h - H_2 sinter plus 2350°C - 1.5 h - vac sinter density.

Fig. 15. Effect of additive on green density of Type B structure.

Fig. 16. Effect of additive on intermediate sinter density of Type B structure.

Fig. 17. Effect of additive on final sinter density of Type B structure.

was a retrogression in the sintered density of the ThO_2 -doped samples compacted at 40,000 psi; these samples had also behaved differently in the green state. The exact reason for this behavior is not known at this time and will be studied in more detail in the future.

Linear and Diametral Shrinkage

The linear and diametral shrinkages between the green and final sintered condition were calculated; the results are presented in Table II. Figure 18 shows the data for selective lots which reflect the influence of FSS size for the undoped and doped powders of Type B morphology. The data as a function of particle size for all four powder lots having Type C morphology are shown in Fig. 19.

The data show that material transport during sintering depends primarily on the particle size of the Type B powders. The rate of densification, as measured by shrinkage for this type powder, increases with decreasing FSS size. This is not true, however, for Type C powders. The shrinkage of the Type C powders corresponds nearly to that of the 2.31μ , Mo-36 powder having a Type B structure, regardless of starting particle size.

Because of high activity and large amounts of contact areas, the finer powder compacts shrink more than the coarse powder compacts; the coarse powders have less contact area for diffusion and less activity during sintering. In all cases shown, the diametral shrinkage is slightly greater than the linear shrinkage, with the least spread occurring for the Type C powders.

The curves for the 4.15μ , Mo-17 powder which contained ThO_2 look nearly identical to those for the 4.0μ , Mo-20 powder which had no ThO_2 . The coarser powder, 6.70μ , Mo-3, containing ThO_2 behaved quite differently than the coarser powder, 5.9μ , Mo-18, which contained no ThO_2 , with the shrinkages being less than half that for the sample containing no ThO_2 .

At LASL we have been able to correlate specific surface with densities as a function of process history. Figures 20 and 21 show these data for 10,000- and 80,000-psi compact pressures, respectively. The curves for the specimens compacted at 10,000 psi appear to be somewhat more erratic than for those pressed at 80,000 psi. Nevertheless, a correlation is shown for specific surface vs density in the green

and sintered conditions. A fairly flat curve exists for both sintering conditions over the particle range 2.31 to 4.3μ (specific surface 0.255 to $0.137 \text{ m}^2/\text{g}$, respectively), dropping off rapidly as the size increased to 5.9μ (specific surface $0.103 \text{ m}^2/\text{g}$). The specific surface of the Type C powder bears little significance to sinterability because it is dependent upon the size of the particles which make up the aggregate.

It may be concluded from the Mo data, as well as that obtained from the NbC powders, that morphology is indeed a very important characteristic of a powder. It is hoped that this parameter will be given more attention by the powder manufacturer and the powder user. It seems evident that by using powder morphology in conjunction with the other characterization data one can plan programs and processes on a more scientific level of understanding.

SUMMARY

Recent developments at LASL have shown that complete characterization, including morphology, is essential to successful and economical use of powders in powder metallurgy fabrication processes. The importance of metallographic examination cannot be overemphasized in the evaluation of other characterization data in the development of procurement specifications.

Much trial and error can be eliminated through better understanding and use of powder characterization data. By classing a powder into a specific morphological type of microstructure, it is possible with some degree of predictability to show a correlation between parameters such as average particle size and specific surface with the density of green and sintered compacts. A dense discrete particle, Type B, as a function of grain size, offers some degree of predictability relative to sintered density. An aggregate particle, Type C, is less predictable because it is dependent upon the size of the individual particles which make up the aggregate.

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Fig. 18. Effect of particle size and additives on the linear and diameter shrinkage of selective Mo powder lots having Type B structure.

Fig. 19. Effect of particle size on the linear and diameter shrinkage of all Mo powder lots having Type C structure.

Fig. 20. Effect of specific surface on density of the Type B structure as a function of FSS and process history; all samples compacted at 10,000 psi.

Fig. 21. Effect of specific surface on density of the Type B structure as a function of FSS and process history; all samples compacted at 80,000 psi.