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TECHNICAL NOTE 2731

INFLUENCE OF STRUCTURE ON PROPERTIES OF SINTERED CHROMIUM CARBIDE

By H. J. Hamjian and W. G. Lidman

Lewis Flight Propulsion Laboratory
Cleveland, Ohio

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By H. J. Hamjian and W. G. Lidman

SUMMARY

An investigation was conducted to study the influence of structural variations on the properties of chromium carbide sintered under pressure. The results show that the room-temperature strength and hardness are influenced by the stages of sintering, which are defined by grain size and by the number, size, location, and shape of pores. The extent to which sintering has progressed during the second stage, when densification occurs, and the sintering conditions which will yield optimum room-temperature strength can be determined from hardness. It was found that coarse-grained structures are detrimental to room-temperature strength. On the basis of limited data, coarse-grained structures may not be detrimental at elevated temperatures.

INTRODUCTION

The structure and the properties of metals and alloys are dependent upon the many variables encountered in the casting and forging practices employed. In the fabrication of materials by powder metallurgical techniques, structure and properties are dependent upon such sintering variables as pressure, time, and temperature, which might be considered analogous with the processing variables of casting or forging.

Results of a recent investigation of chromium carbide sintered under pressure (reference 1) showed that the grain size after sintering is time and temperature dependent; thus it is possible to attain the same grain size resulting from a certain given time t_1 and temperature T_1 by using another combination of time t_2 and temperature T_2. The sintering process was divided into three stages. The welding or bonding together of particles, referred to as the first stage, was studied by Kuczynski (reference 2). The portion of the sintering cycle during which grain size and density appeared to be interdependent is designated as the second stage of sintering. Continued sintering after maximum

density was reached resulted in further grain growth; this is designated as the third stage of sintering. It is shown that the second and third stages of sintering could be identified through structural appearances such as grain size and the number, location, shape, and size of the pores within the sample. Such structural changes can affect the physical properties of materials; consequently, it is desirable to correlate properties with the structure of the material and stages of sintering rather than with arbitrary sintering temperatures and time at temperature. 2524

The purpose of this investigation is to correlate structural changes observed during sintering with strength and hardness of chromium carbide. The specimens investigated were prepared at the NACA Lewis laboratory by sintering under pressure, and the structure was altered from specimen to specimen by varying the temperature, the time at temperature, or the pressure.

APPARATUS AND PROCEDURE

Fabrication of Specimens

X-ray diffraction analysis of the chromium carbide powder, which was obtained from a commercial source, showed the composition to be Cr_3C_2. Particle-size measurements were made with a microscope having a calibrated filar eyepiece and the average initial particle size was 6.0 microns.

Specimens were prepared by sintering under pressure in a manner similar to the method described in reference 1. Eighty grams of chromium carbide powder was heated by induction in the specimen chamber $\left(1\frac{13}{16}\text{-in. diam.}\right)$ of a graphite die (6 in. diam. and 5 in. length). Specimen disks that were approximately 1/4-inch thick were formed. Pressure was applied to the specimen during the sintering cycle through a lever system with a ratio of 24. The sintering temperature was measured with an optical pyrometer sighted between two loops of the induction coil into a 3/8-inch hole drilled 1 inch deep into the midsection of the die. With the apparatus used and under these conditions, the maximum variation of the die temperature was $\pm 10^{\circ}$ F.

The power to the induction coil was so adjusted that the die and the specimen could be heated to 2500° F in 20 minutes; no increase in grain size was observed within 1 minute. Less than 2.5 minutes was required to heat from this temperature to 3000° F. The effects of time and temperature on structure and properties were investigated with a series of specimens sintered under a pressure of 2000 pounds per

square inch. Sintering temperatures for this portion of the investigation were increased in increments of 100° F from 2500° to 3000° F; the sintering periods ranged from 5 minutes to 90 minutes at temperatures of 2800° F and above, and from 5 to 360 minutes at 2500°, 2600°, and 2700° F.

The effects of pressure during sintering on the structure and the properties of this material were investigated with additional samples, all of which were sintered at 2800° F for 45 minutes, but with various pressures applied in one of the following sequences: (a) total load under investigation applied at room temperature and maintained during heating and at sintering temperature for duration of the sintering time, (b) zero load applied during heating portion of cycle; various constant loads applied at sintering temperature for duration of the sintering time, (c) partial load applied at room temperature and maintained during heating portion of cycle; load increased to 2000 pounds per square inch at sintering temperature and held for duration of sintering time. The following pressures were used for this portion of the investigation: 0, 110, 600, 1000, 2000, and 3000 pounds per square inch.

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Analysis of Specimens

Two rectangular modulus-of-rupture samples were ground with diamond-impregnated wheels from each hot-pressed specimen disk. The finished dimensions were 0.2 inch thick, 0.4 inch wide, and approximately $1\frac{3}{4}$ inches long. Specimens were evaluated at room temperature by use of a three-point loading apparatus with a $1\frac{1}{2}$-inch span between specimen supports.

In order to correlate the effect of structure on short-time elevated-temperature strength properties, additional modulus-of-rupture samples, having grain sizes of 12.5 and 18.3 microns, were prepared for evaluation at 1800°, 2000°, 2200°, and 2400° ±10° F. The apparatus and procedure were similar to those described in reference 3. A commercial electric furnace was modified to incorporate a lever-loading system. Silicon carbide knife edges spaced $1\frac{1}{2}$ inches apart supported the specimen, and load was applied at its center by a third knife edge fastened to the loading system. Loading was so adjusted that the calculated stress increase was 2000 pounds per square inch per minute.

Density measurements were made on pieces of the modulus-of-rupture bars that were broken at room temperature. An analytical balance was used for weighing the samples in air, and when suspended in water. The apparent density of each sample reported in this investigation was reproducible within ±0.01 gram per milliliter.

Four Rockwell A hardness readings were taken on one-half of each modulus-of-rupture bar after evaluation at room temperature. These measurements were equally spaced from the center (near the fractured surface) to the outer end of the piece, and the average of all four was used for the comparison between samples.

2524

Grain sizes were determined from pieces cut from the center of each specimen. In preparation, each piece was polished with diamond abrasives and etched to reveal the grains with a 1:1 mixture of 20-percent potassium hydroxide and 20-percent potassium ferricyanide heated to 160° F. The maximum dimension of all well defined grains was measured in 8 by 10 prints of representative areas photographed at 1000 diameters. Measurements of the 15 largest grains were averaged to determine the sample grain size, on the assumption that the largest grains were among the first to begin growth and consequently would give a comparison of grain growth among samples.

RESULTS AND DISCUSSION

Structural changes of sintered chromium carbide were observed in reference 1 when either sintering temperature or time at temperature was altered. It was noted that in the second stage of sintering, density and grain size are related. The pores become smaller, fewer in number, tend to spheroidize, and are located in the grain boundaries, while the grains increase in size. In the third stage of sintering, grain growth continues although there is no appreciable increase in density; the pores tend to be located within the grains, the pores are spherical, and grain growth is more rapid. Figures 1 and 2, reproduced from reference 1, show the effect of sintering temperature and time at temperature, at constant pressure, on the grain size, pore volume, and distribution of pores in sintered chromium carbide.

The effect of pressure during sintering (temperature and time at temperature held constant) on the structure can be observed from photomicrographs of representative samples (fig. 3). The samples were prepared at 2800° F for 45 minutes under different conditions of pressure. These photomicrographs show that grain size and density are affected by the applied pressure. Data which show the effect of various pressures when applied at room temperature and maintained throughout the sintering cycle are presented in table I. These data are plotted in figure 4 and demonstrate the effect of pressure on the structure, as represented by grain size and apparent density (degree of porosity), and on the properties, as represented by modulus-of-rupture and hardness.

The specimens sintered with zero applied pressure (loose powder) crumbled readily, were too porous for reliable density and hardness data, and were too friable for further analysis. With an applied

2524

pressure of 110 pounds per square inch, the specimen was porous and soft but sufficiently coherent for strength and hardness determination. Additional specimens were fabricated at 3000° and 3200° F to determine whether sintering could be achieved at higher temperatures with 110 pounds per square inch applied load. The specimen sintered at 3000° F was cracked on removal from the die but similar in appearance and characteristics to that prepared at 2800° F. Upon removal from the die, the specimen heated to 3200° F was fractured and showed evidence of melting, which resulted in large crystals. Rapid rates of increase in hardness and modulus-of-rupture properties are observed when the pressure is increased to 600 pounds per square inch. Increasing the pressure to 3000 pounds per square inch resulted in smaller improvements. From this it appears that to fabricate a sound product, a certain minimum pressure is required during sintering to provide sufficient initial contact between particles to permit grain growth and densification.

Data which show the effect of applying different pressures for only the time period during which the specimen is at the sintering temperature are presented in table II. The effects of applying different pressures while heating to the sintering temperature and of then increasing each pressure to 2000 pounds per square inch and maintaining this load while at the sintering temperature are shown in table III. These results indicate that there is only a small difference in properties or structures because of the sequence in which the load is applied, provided that the maximum load is the same in all cases and is maintained throughout the time at sintering temperature.

The effect of structure (grain size and apparent density), produced by sintering under different time, temperature, and pressure conditions, on such physical properties as strength and hardness is indicated by the data in table IV. In order to show more clearly the apparent trends in the data and the correlation between structure and physical properties of all the samples, these data have been plotted along with the variable pressure data in figures 5 to 9. Because of the nature of the properties investigated, the trends are shown as bands.

The correlations of grain size and density with the room-temperature modulus-of-rupture strength of the samples are shown in figures 5 and 6. Strength increases as the grain size of the sintered sample increases (fig. 5) until a maximum is reached when the grain size is approximately 11 microns, and then with larger grain sizes, the strength decreases. Figure 6 shows that up to near maximum density, strength improves as density increases and then beyond this value, which occurs at about 6.50 grams per milliliter, the strength falls off rapidly. Density increases as grain size increases and the pores are in the grain boundaries during the second stage of sintering. In the

third stage of sintering, at near maximum density, the grain size continues to increase and pores are located within the grains (reference 1). As the second stage of sintering progresses it is accompanied by an increase in strength (figs. 5 and 6). A peak in strength occurs at the transition between the second and the third stages and then strength decreases with increasing grain size while there is no appreciable change in density.

An increase in strength during the second stage of sintering can be accounted for by the decrease in size and number and by the change in location of the pores. In the third stage of sintering when the remaining pores are located within the grains, there is no appreciable change in the pore size or number since near maximum density has been attained, but the grains continue to grow. The effect of large grains in the sintered samples is apparently detrimental to the room-temperature strength, and this effect overshadows any improvement that can be gained by the slight increase in density.

The variation in hardness with grain size and density is shown in figures 7 and 8. Observations of the indentations made by the Rockwell hardness tester showed evidence of plastic deformation in the chromium carbide rather than crumbling of the grains as is the case with some carbide materials. This behavior of the material under investigation probably accounts for the consistent hardness values obtained, and also contributes to the reliability of the data. In most cases the four-position traverse of each sample from the center to the end showed no trend in hardness across the sample (table IV); consequently, the averages plotted are representative values. Curves similar in shape to those obtained for the modulus-of-rupture evaluations were obtained and show that hardness increases with increasing grain size and density; a maximum is reached with a grain size of approximately 11 microns and near maximum density, and then the hardness tends to decrease. The values of grain size and density at which maximum hardness first occurs correspond to the transition between the second and third stages of sintering just as with the maximum values of room-temperature strength shown in figures 5 and 6.

A plot of the modulus-of-rupture and hardness data is shown in figure 9. The trend indicates increasing strength with increasing hardness during the second stage of sintering. These results suggest that for materials which give reliable hardness values, hardness, a property which is convenient to measure, may be used as an indication of the extent to which sintering has progressed during the second stage as well as to establish the sintering conditions which will produce material having optimum room-temperature strength.

The effect of structure on elevated-temperature strength was investigated. Specimens sintered to the transition between the second

and third stages, having a density of 6.46 grams per milliliter and a grain size of 12.5 microns, were compared with material sintered in the third stage, having a density of 6.65 grams per milliliter and a grain size of 18.3 microns. The data from this portion of the investigation are listed in table V and are plotted against evaluation temperature in figure 10. The fine-grained material with lower density has room-temperature strength superior to that of the coarse-grain material with the higher density. At elevated temperatures, there is a possibility as in other materials that the relative strengths would reverse and coarse-grained structures would be stronger. The strength of both structures greatly improved over the room-temperature strength. This might be a result of slight increases in ductility which would reduce the effect of stress concentrations for evaluations at 1800°, 2000°, and 2200° F. Modulus-of-rupture data for the coarse-grained material were higher than for the fine-grained material at 1800°, 2200°, and 2400° F. If grain-size effects are significant, long-time properties should demonstrate such structural effects more clearly.

2524

RESULTS AND CONCLUSIONS

An investigation of the influence of structural variations on properties of chromium carbide sintered under pressure has indicated that:

1. Strength and hardness are related to the stages of sintering. These properties increase during the second stage when the pores are in the grain boundaries and are reducing in size and number; after the transition between the second and third stages, both properties tend to decrease as the grain size continues to increase.

2. The room-temperature strength and hardness of chromium carbide are influenced by the grain size and by the number, size, location, and shape of pores.

3. Coarse-grained structures are detrimental to room-temperature strength, and their effects overshadow the slight increases in density which accompany these structures in the third stage. On the basis of limited data, coarse-grained structures may not be detrimental at elevated temperatures.

4. Hardness data may be used to determine the extent to which sintering has progressed during the second stage as well as to establish the sintering conditions which will yield optimum room-temperature strength.

Lewis Flight Propulsion Laboratory
National Advisory Committee for Aeronautics
Cleveland, Ohio, March 28, 1952

REFERENCES

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2. Kuczynski, G. C.: Self-Diffusion in Sintering of Metallic Particles. Trans. A.I.M.E., vol. 185, no. 2, Feb. 1949, pp. 169-178.

3. Lidman, W. G., and Hamjian, H. J.: Properties of a Boron Carbide-Iron Ceramal. NACA TN 2050, 1950.

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TABLE I - EFFECT OF PRESSURE APPLIED AT ROOM TEMPERATURE AND MAINTAINED THROUGHOUT SINTERING CYCLES AT 2800° F FOR 45 MINUTES

Applied pressure (lb/sq in.)	Modulus-of-rupture at 80° F (lb/sq in.)	Density (g/ml)	Grain size (microns)	Hardness, Rockwell A				
				1	2	3	4	Av.
0	Soft and powdery	----	-----	----	----	----	----	----
110	8,500	----	-----	25.9	26.8	26.1	24.5	25.8
600	34,700	6.14	9.90	83.4	83.4	83.1	83.7	83.5
1000	44,600	6.42	11.80	89.7	89.5	89.1	89.1	89.4
2000	49,200	6.57	13.20	92.0	91.7	91.9	91.2	91.7
3000	49,600	6.66	13.70	91.9	92.1	92.2	92.2	92.1

TABLE II - EFFECT OF PRESSURE APPLIED AT SINTERING TEMPERATURE OF 2800° F FOR 45 MINUTES

Applied pressure at sintering temperature (lb/sq in.)	Modulus-of-rupture at 80° F (lb/sq in.)	Density (g/ml)	Grain size (microns)	Hardness, Rockwell A				
				1	2	3	4	Av.
0	Soft and powdery	----	-----	----	----	----	----	----
2000	43,400	6.48	12.90	90.9	90.8	90.3	90.5	90.6
3000	39,700	6.58	13.40	90.8	90.7	91.1	91.2	91.0

TABLE III - EFFECT OF PARTIAL PRESSURE AT ROOM TEMPERATURE WITH 2000 POUNDS PER SQUARE INCH AT SINTERING TEMPERATURE OF 2800° F FOR 45 MINUTES

Applied pressure at room temperature	Modulus-of-rupture at 80° F (lb/sq in.)	Density (g/ml)	Grain size (microns)	Hardness, Rockwell A				
				1	2	3	4	Av.
0	43,400	6.48	12.90	90.9	90.8	90.3	90.5	90.6
200	42,600	6.57	13.20	91.8	92.0	92.1	92.1	92.0
1000	41,900	6.59	13.40	91.5	91.0	91.2	91.5	91.3
2000	49,200	6.57	13.20	92.0	91.7	91.9	91.2	91.7

TABLE IV - DENSITY, GRAIN SIZE, MODULUS-OF-RUPTURE, AND HARDNESS OF CHROMIUM CARBIDE SPECIMENS SINTERED UNDER PRESSURE OF 2000 POUNDS PER SQUARE INCH

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Sintering time (min)	Density (g/ml)	Grain size (microns)	Average modulus-of-rupture at room temperature (lb/sq in.)	Hardness, Rockwell A				
				1	2	3	4	Av.
(a) Sintering temperature, 2500° F.								
5	5.38	6.50	25,400	71.5	71.6	71.2	69.9	71.0
15	5.66	7.30	24,300	73.8	73.6	73.9	73.7	73.8
30	5.88	7.70	22,700	74.3	74.0	74.0	74.2	74.1
45	5.94	8.20	38,600	86.2	86.2	86.3	85.3	86.0
90	6.03	8.50	40,000	84.7	89.1	86.7	86.5	86.8
180	6.12	9.40	49,900	86.0	86.8	87.2	88.1	87.0
360	6.43	9.90	55,000	91.0	90.8	90.8	90.4	90.8
(b) Sintering temperature, 2600° F.								
5	5.54	8.05	26,000	70.5	70.8	70.0	68.8	70.0
15	5.98	8.95	37,200	84.2	84.2	84.0	85.2	84.4
30	6.04	9.75	38,700	83.2	83.5	84.0	84.8	83.9
45	6.12	10.05	36,300	85.3	86.0	87.0	88.2	86.6
90	6.30	10.60	44,100	89.7	90.2	90.0	91.3	90.3
180	6.59	11.40	57,000	91.0	91.0	91.1	91.0	91.0
360	6.64	11.80	53,900	92.1	92.2	92.1	92.1	92.1
(c) Sintering temperature, 2700° F.								
5	5.99	8.65	38,400	82.8	82.5	83.0	84.8	83.3
15	6.11	9.95	44,000	86.8	87.1	87.3	87.9	87.3
30	6.12	10.75	43,900	89.6	90.0	90.6	91.8	90.5
45	6.37	11.10	53,900	89.2	89.1	89.0	89.0	89.1
90	6.42	11.50	46,600	88.8	89.5	89.3	90.0	89.4
180	6.66	13.02	51,600	92.0	92.0	92.0	92.3	92.1
360	6.65	15.00	48,000	92.1	92.2	92.1	92.3	92.2
(d) Sintering temperature, 2800° F.								
5	6.04	9.10	42,600	86.5	87.2	87.5	88.5	87.4
15	6.34	10.80	40,400	90.4	90.3	91.0	90.3	90.5
30	6.57	12.35	47,500	91.1	90.9	91.1	91.1	91.0
45	6.57	13.20	49,200	92.0	91.7	91.9	91.2	91.7
90	6.61	14.90	44,900	91.8	91.9	92.1	92.2	92.0

2524

TABLE IV - DENSITY, GRAIN SIZE, MODULUS-OF-RUPTURE, AND HARDNESS OF CHROMIUM CARBIDE SPECIMENS SINTERED UNDER PRESSURE OF 2000 POUNDS PER SQUARE INCH - Concluded.

Sintering time (min)	Density (g/ml)	Grain size (microns)	Average modulus-of-rupture at room temperature (lb/sq in.)	Hardness, Rockwell A				
				1	2	3	4	Av.
(e) Sintering temperature, 2900° F.								
5	6.10	11.20	46,000	89.9	90.9	91.2	91.8	91.0
15	6.46	12.50	48,300	91.1	91.1	91.0	91.8	91.2
30	6.65	15.20	38,400	91.7	91.8	91.8	91.4	91.7
45	6.65	16.40	37,400	91.7	91.6	91.2	91.3	91.4
90	6.65	18.35	36,000	91.3	91.7	91.0	91.2	91.3
(f) Sintering temperature, 3000° F.								
5	6.62	12.75	38,800	91.0	90.8	90.3	90.5	90.65
15	6.61	15.90	30,000	89.2	89.1	89.0	89.0	89.1
30	6.64	18.60	26,000	86.3	86.2	87.8	88.0	87.1
45	6.64	19.10	24,900	88.0	88.7	88	88.1	88.2
90	6.65	21.40	------	----	----	----	----	----

TABLE V - COMPARISON OF GRAIN SIZE WITH ROOM- AND ELEVATED-TEMPERATURE STRENGTH FOR CHROMIUM CARBIDE SINTERED UNDER PRESSURE OF 2000 POUNDS PER SQUARE INCH

Sintering temperature (°F)	Sintering time (min)	Density (g/ml)	Grain size (microns)	Evaluation temperature (°F)	Average modulus-of-rupture (lb/sq in.)
2900	15	6.46	12.5	80	48,300
2900	15	6.46	12.5	1800	71,700
2900	15	6.46	12.5	2000	83,700
2900	15	6.46	12.5	2200	57,300
2900	15	6.46	12.5	2400	30,200
2900	90	6.65	18.35	80	36,000
2900	90	6.65	18.35	1800	84,500
2900	90	6.65	18.35	2000	73,202
2900	90	6.65	18.35	2200	63,100
2900	90	6.65	18.35	2400	35,700

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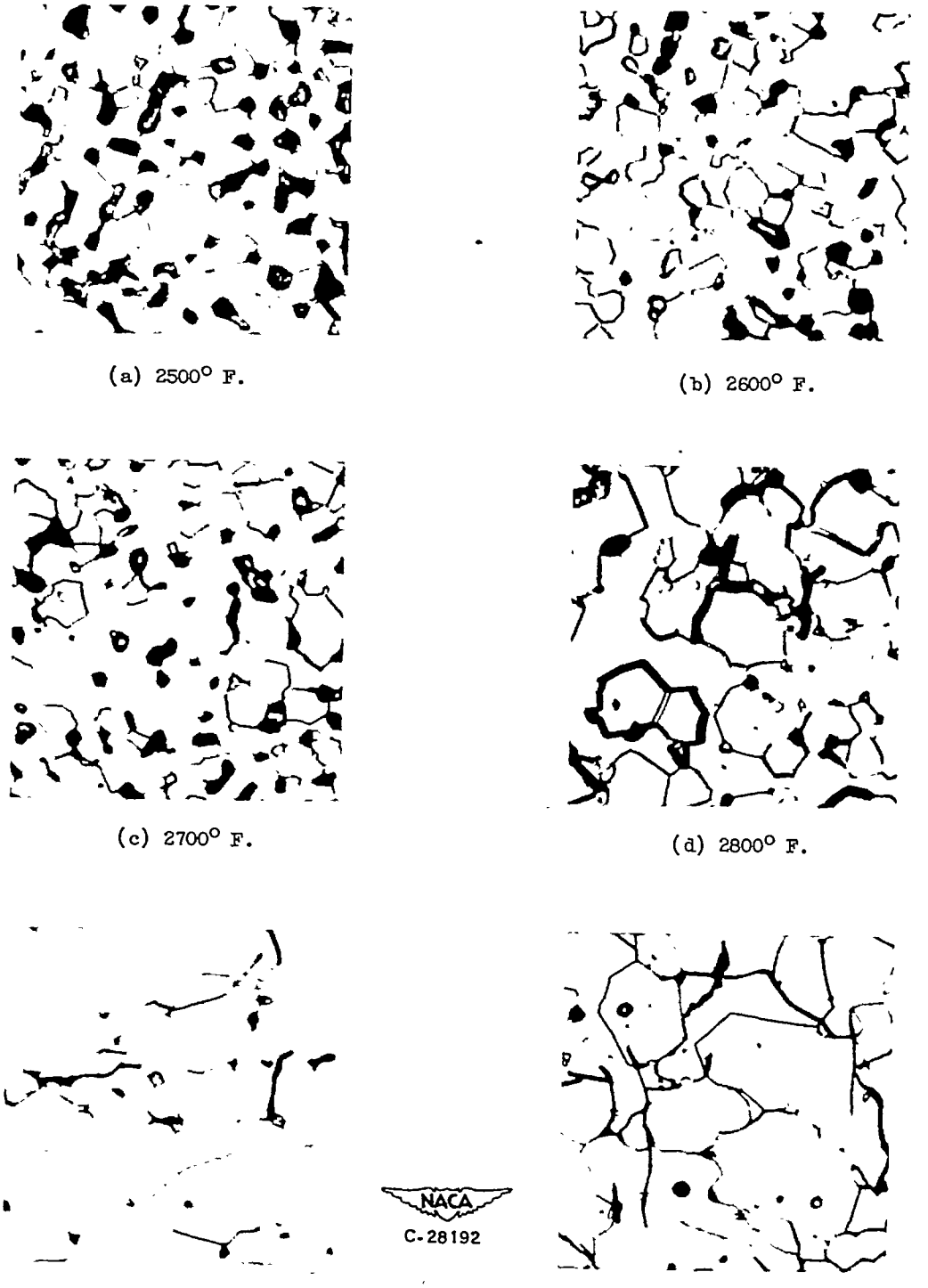

(a) 2500° F.

(b) 2600° F.

(c) 2700° F.

(d) 2800° F.

(e) 2900° F.

(f) 3000° F.

Figure 1. - Photomicrographs of specimens sintered at various temperatures for 90 minutes. X1000.

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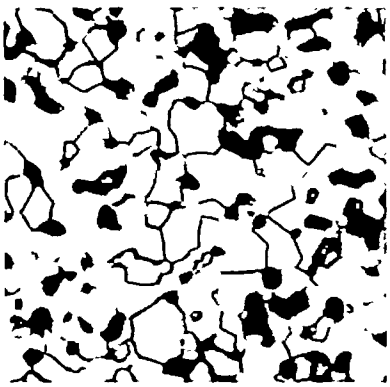
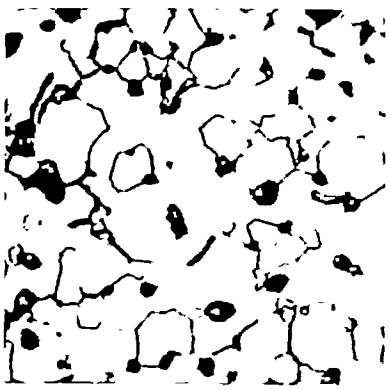
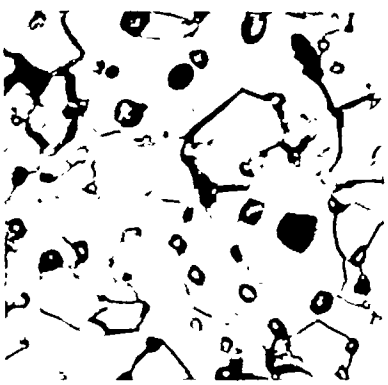


(a) 5 minutes.

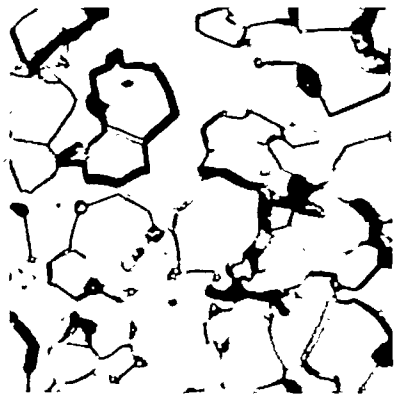


(b) 15 minutes.

(c) 30 minutes.



(d) 45 minutes.



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(e) 90 minutes.

Figure 2. - Photomicrographs of specimens sintered at 2800° F for various times. X1000.

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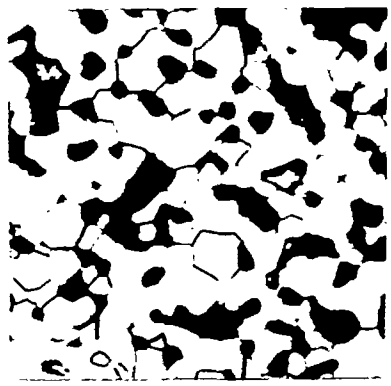
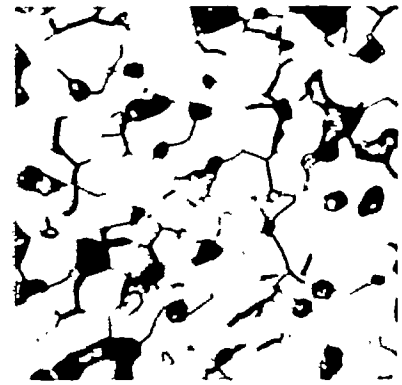
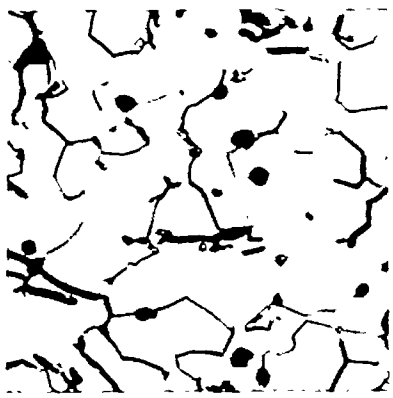


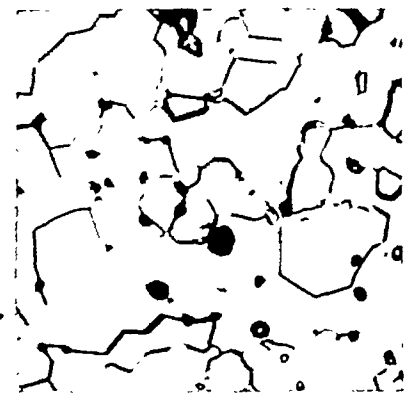
(a) 600 pounds per square inch.



(b) 1000 pounds per square inch.



(c) 2000 pounds per square inch.



(d) 3000 pounds per square inch.

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Figure 3. - Photomicrographs of specimens sintered at 2800° F for 45 minutes under various loads. X1000.

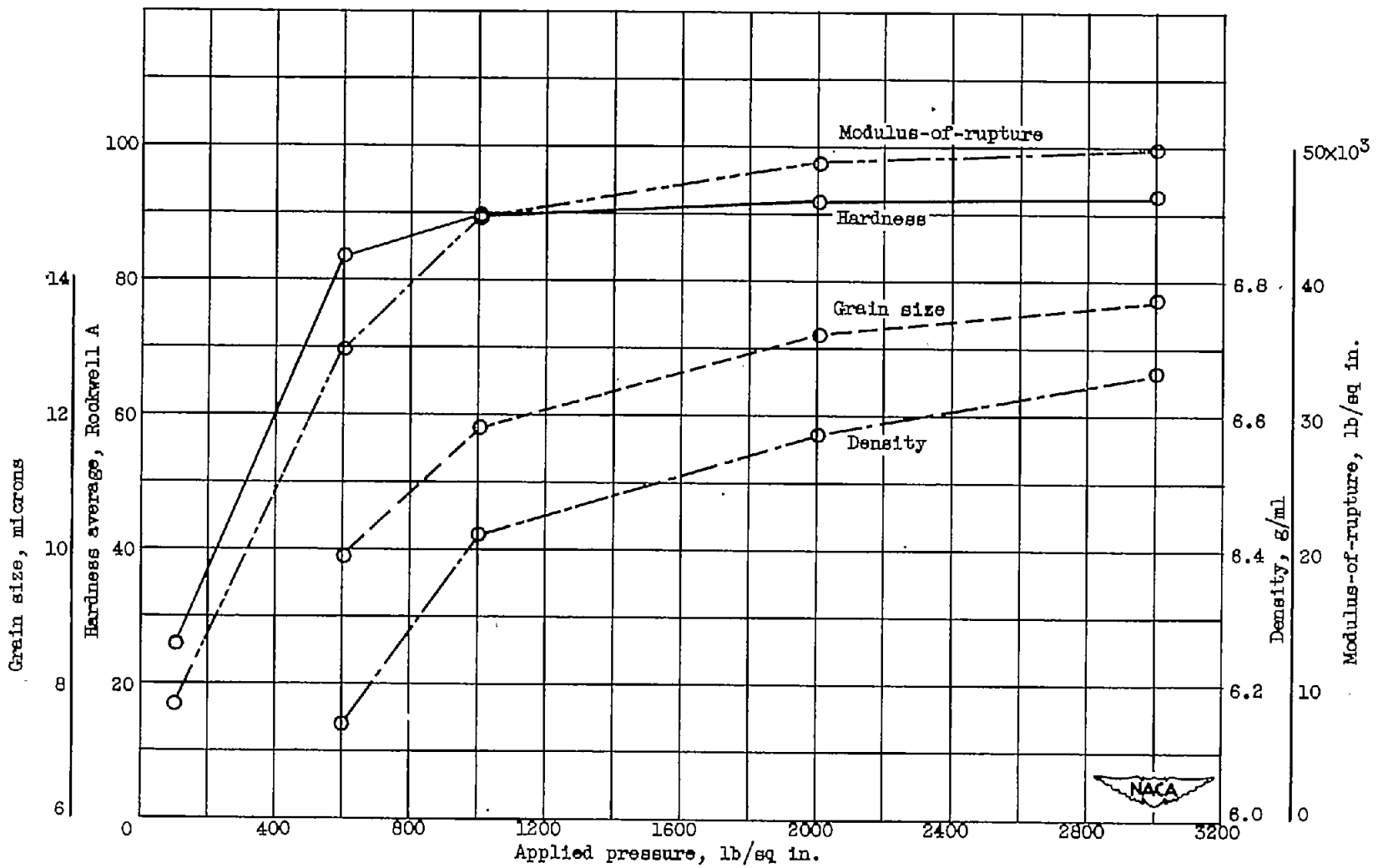

Figure 4. - Variation of properties of chromium carbide at room temperature with applied sintering pressure when sintered at 2800° F for 45 minutes.

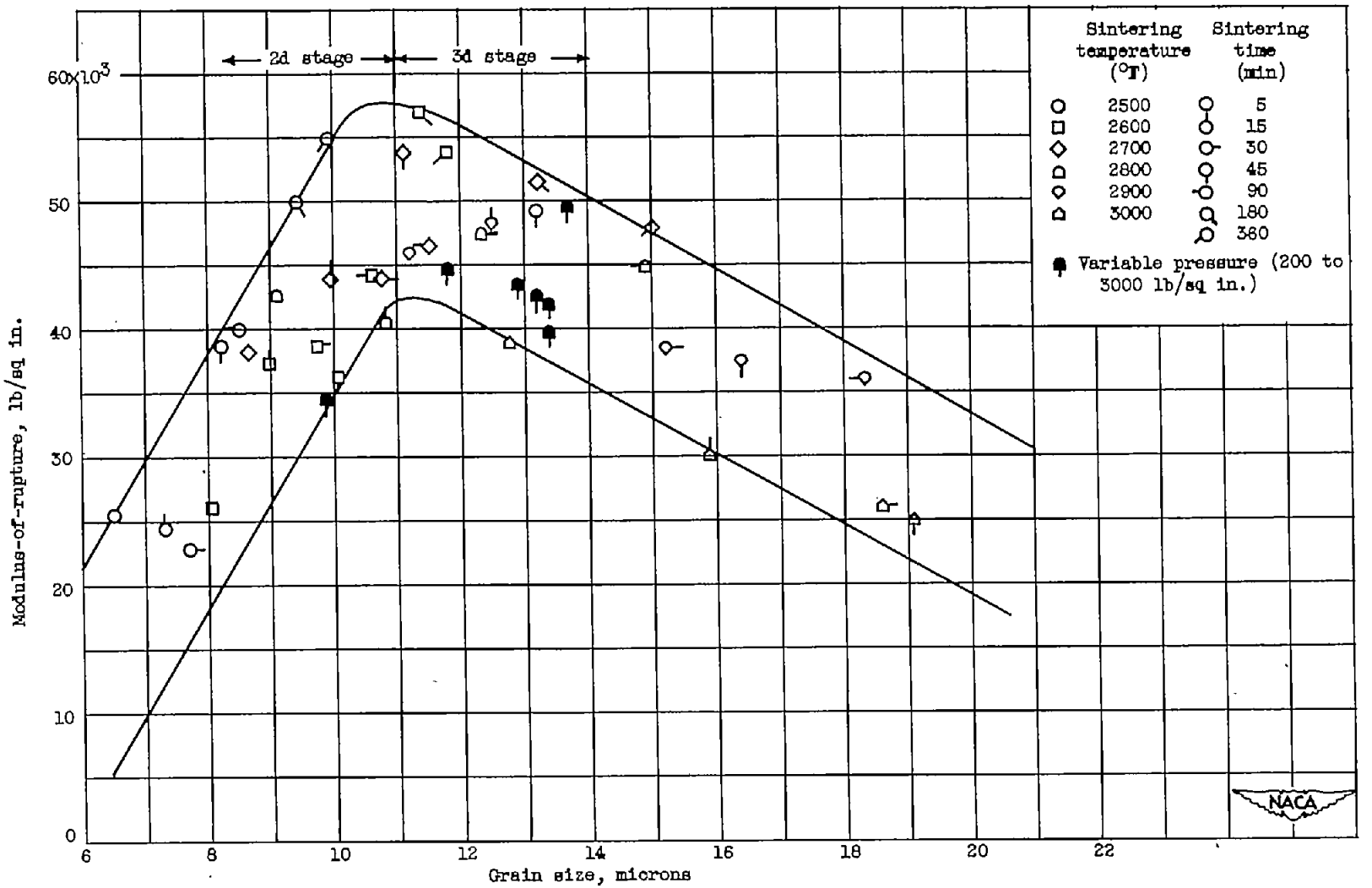

Figure 5. - Variation of room-temperature modulus-of-rupture with grain size and sintering stage for chromium carbide. Sintering pressure, 2000 pounds per square inch.

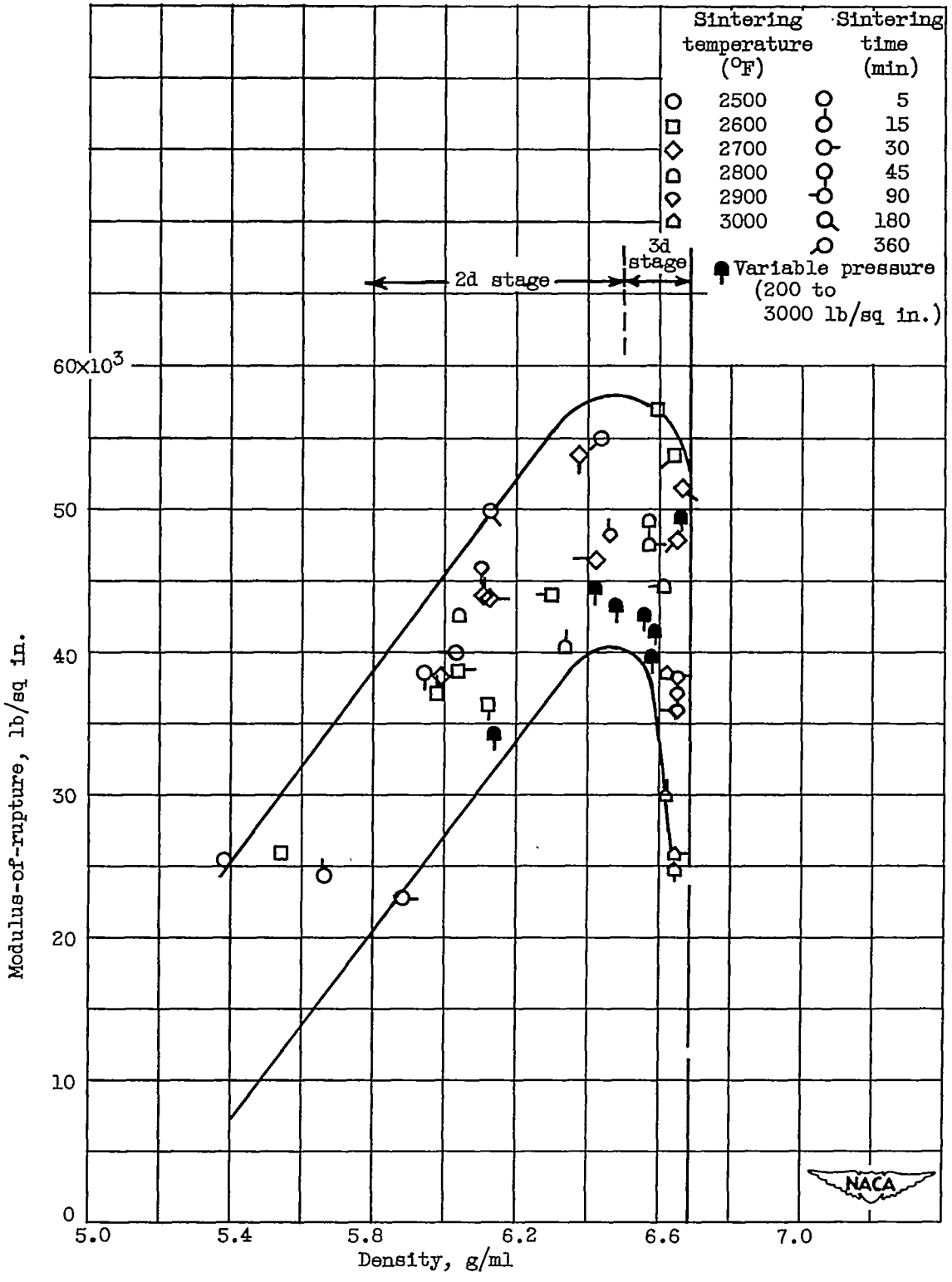

Figure 6. - Variation of modulus-of-rupture with sintered density for chromium carbide. Sintering pressure, 2000 pounds per square inch.

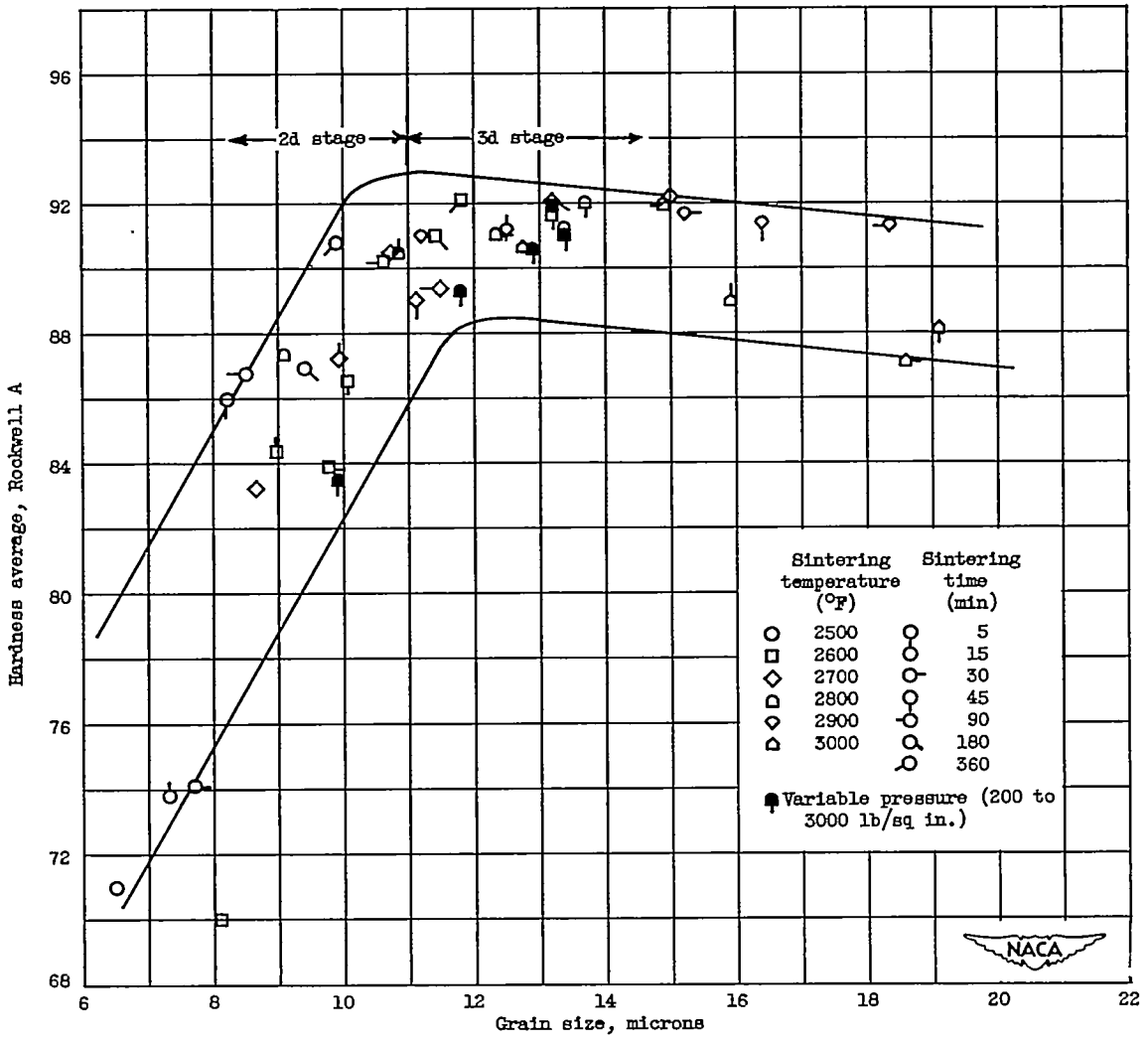

Figure 7. - Variation of hardness with grain size and sintering stage. Sintering pressure, 2000 pounds per square inch.

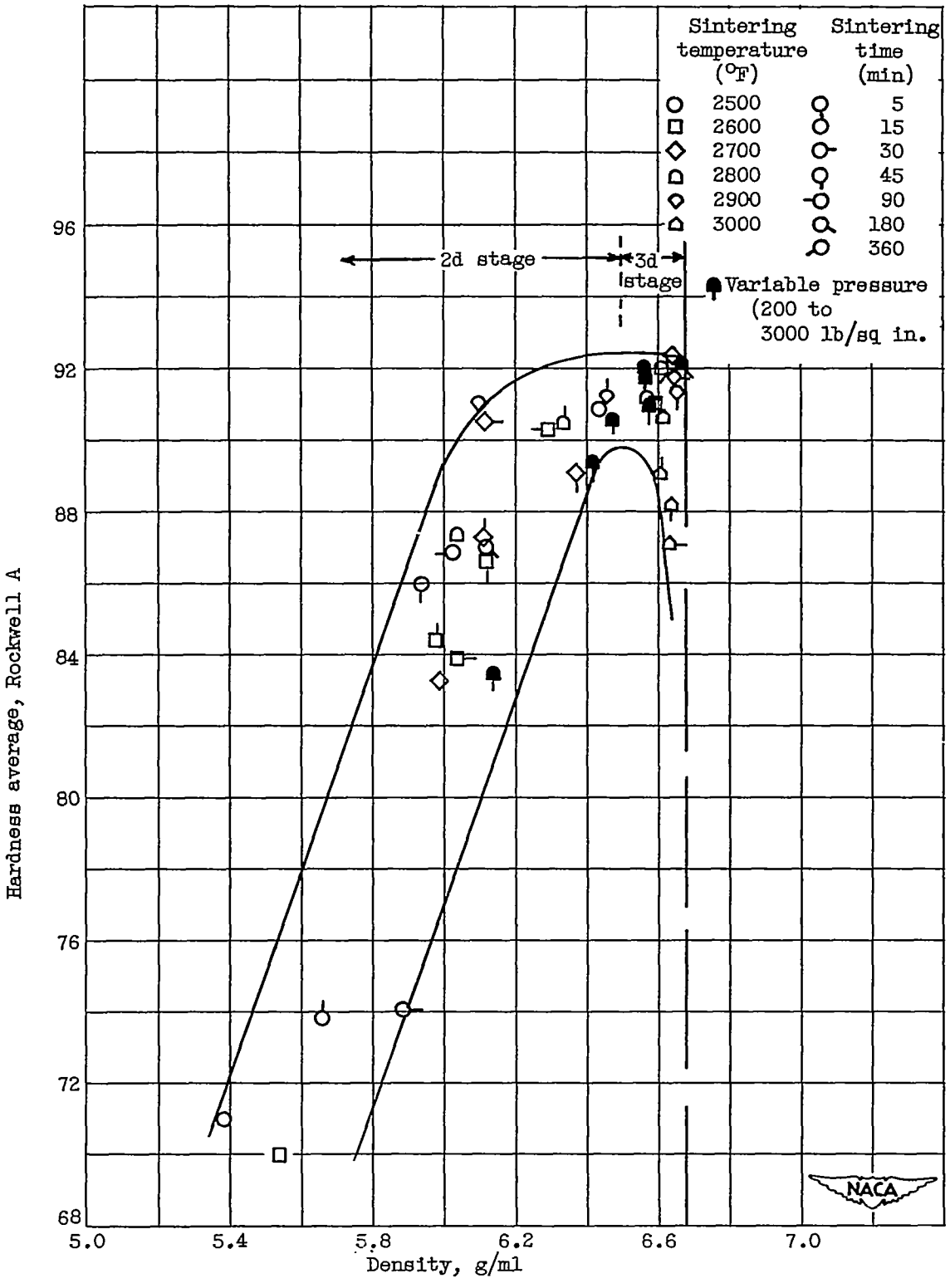

Figure 8. - Variation of hardness with sintered density. Sintering ing pressure, 2000 pounds per square inch.

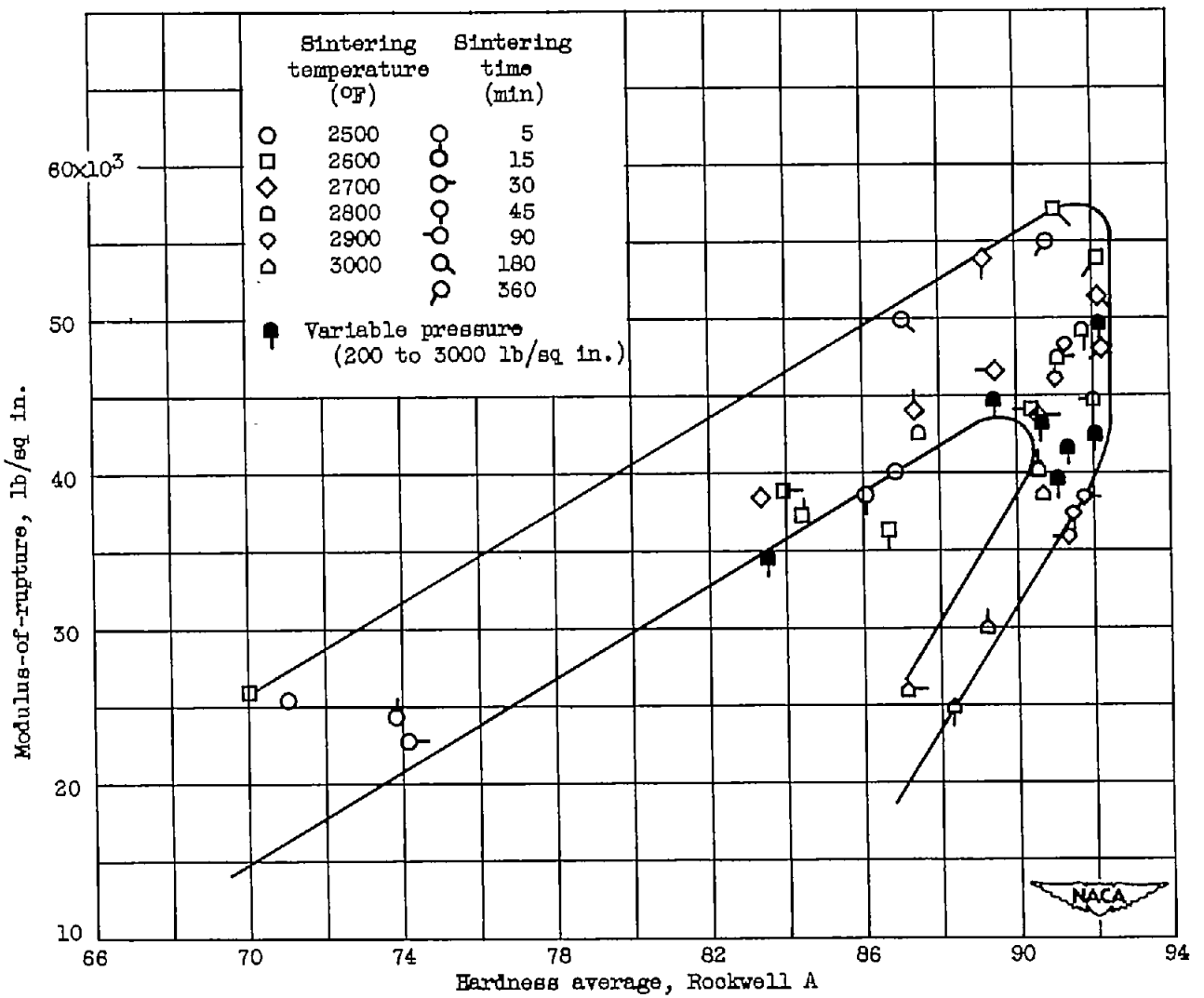

Figure 9. - Variation of room temperature modulus-of-rupture with hardness. Sinter-pressure, 2000 pounds per square inch.

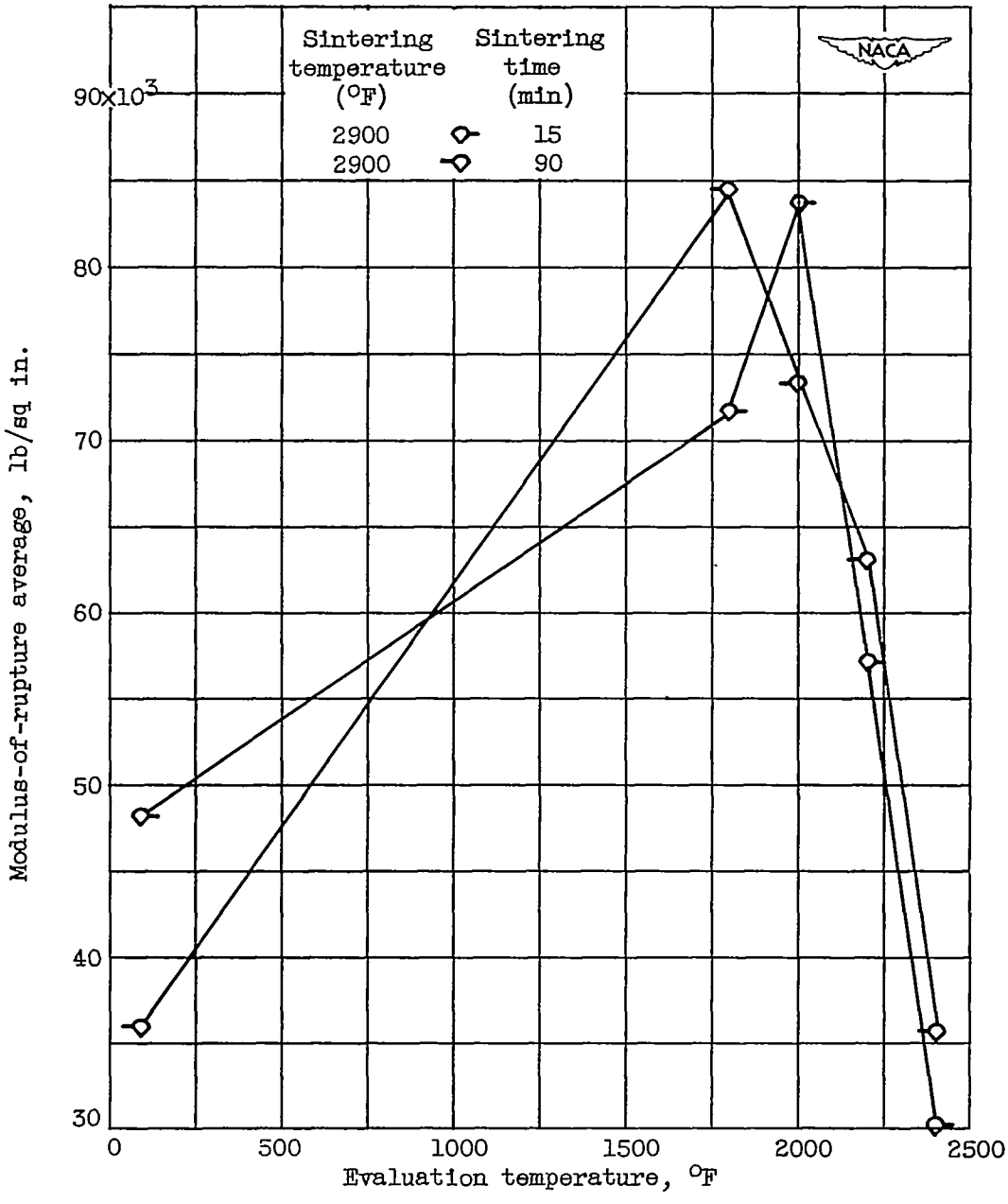

Figure 10. - Variation of large- and small-grain chromium carbide at room- and elevated-temperature modulus-of-rupture strength.

NACA-Langley - 6-23-52 - 1000