EFFECT OF SINTERING TIME AND COOLING RATE ON SINTER HARDENABLE MATERIALS

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ABSTRACT

Sinter hardening is a cost-effective process that combines sintering and heat treatment in one step. It is known that the cooling rate following sintering greatly affects material microstructures, which determine the final properties of sinter hardened materials.

This study investigates the properties of three sinter hardenable materials (two Cr/Mo prealloys and a Ni/Mo prealloy) under various sintering times and cooling rates. The objective is to understand how these sintering conditions influence the development of martensite in the microstructure and control the mechanical properties of the materials. By understanding how sintering and cooling affect these parameters, it is possible to optimize the sintering cycle for individual materials and applications.

INTRODUCTION

Sinter hardening combines sintering and heat treatment in one step by increasing the cooling rate following sintering. High hardness and strength are obtained while minimizing the number of processing steps. The type and amount of alloying elements, the time spent at the sintering temperature, and the post-sintering cooling rate all affect the amount of martensite and bainite in the microstructure. Increasing the cooling rate causes more austenite to transform to martensite. The addition of alloying elements improves hardenability, allowing the martensite transformation to occur at slower cooling rates than otherwise possible [1].

The microstructure of sinter hardened steels is primarily martensitic. To better understand how sintering conditions affect material microstructure and hence mechanical properties, the percentage of martensite and the microstructural homogeneity were evaluated along with mechanical properties for three sinter hardenable materials at each of three different sintering times and three different cooling rates (total of 27 conditions in test matrix).

EXPERIMENTAL PROCEDURE

Materials

Three sinter hardenable materials were evaluated. Two of the base materials are prealloyed with chromium and molybdenum (Astaloy CrM has 3% Cr and 0.5% Mo, and Astaloy CrL has 1.5% Cr and 0.2% Mo). Elemental copper was added to the Astaloy CrL mix. Graphite was added to both base materials at levels intended to produce a good combination of hardness and strength[2]. The third material is an FLC-4608 (Astaloy A + 2%Cu + 0.8%C), which is a common sinter hardening material containing prealloyed Ni and Mo along with admixed elemental copper and graphite powder. Table I gives the mix compositions.

Table I. Mix Compositions

Grade	Ni* (%)	Mo* (%)	Cr* (%)	Cu (%)	C (%)
Astaloy CrL + 1% Cu	-	0.20	1.5	1	0.75
Astaloy CrM	-	0.50	3.0	-	0.50
FLC-4608	1.9	0.55	-	2	0.80

*Shaded elements are prealloyed

Chromium is very attractive because of its low alloying cost and powerful affect on hardenability. Additionally, alloying with chromium may eliminate or reduce the need for copper in the mix, which is an advantage for recycling, since materials containing copper are difficult to recycle[3].

For each premix, transverse rupture bars (MPIF 41) and tensile bars (MPIF 10) were pressed to a green density of 7.0g/cm³ on a Gasbarre 60-ton press. Table II shows the compaction pressures required to reach 7.0g/cm³. The compaction pressure required to reach the desired density varied considerably between the base materials.

Table II. Compaction pressure required to reach 7.0 g/cm³.

Mix	Compaction Pressure	Total % Metallic Alloying Elements
Astaloy CrL + 1% Cu	550 MPa (39.9 tsi)	2.70
Astaloy CrM	625 MPa (45.3 tsi)	3.50
FLC-4608	550 MPa (39.9 tsi)	4.65

Prealloyed metallic elements decrease the compressibility of the mix due to solution hardening of the iron powder particles. Alloying elements with high hardenability, such as chromium, particularly affect the compressibility, but their hardenability is beneficial for sinter hardening. Admixed copper and graphite have very little effect on compressibility.

Processing conditions

Test bars were sintered at 1120°C (2050°F) in a 90% N_2 / 10% H_2 atmosphere in an Abbott laboratory furnace equipped with a Varicool convection cooling system. Sintering time and cooling rate were varied. Three fan speeds were used to vary the cooling rate (0, 20 or 40 Hz). These speeds will be translated into °C/s. Sintering times were 10, 20, or 40 minutes. For each of the 9 sets of sintering conditions, the three materials were sintered together. After sintering, all samples were tempered for 60 minutes in air at 177°C (350°F) in order to stress relieve the martensite.

Testing

After tempering, mechanical properties were tested, including tensile properties (MPIF 10), transverse rupture strength (MPIF 41), and apparent hardness (MPIF 43). TRS bars were used to evaluate the microstructures and measure the dimensional change (MPIF 44), sintered density (MPIF 42), and sintered carbon level (ASTM E1019-02).

Metallography

Transverse rupture strength bars were prepared for metallographic analysis. Photomicrographs were taken of the microstructures after etching in either Picral or a 50/50 mix of 1% Nital and Picral. The amount of martensite and bainite was determined by point analysis (ASTM E562).

Cooling Rate Determination

Fan speed is only a relative measure of the cooling rate; to determine the actual cooling rate experienced by the parts in °C/sec (or °F/s), sample microstructures were compared to available phase amount diagrams such as the diagram for FLC-4608 shown below in Figure 1. These diagrams are derived from the CCT diagrams of specific materials and analyses of samples cooled at different rates and measured using a dilatometer. The percentages of martensite found in the microstructures of the samples are compared to the diagram to get the cooling rates.

The samples used to develop the CCT diagrams were sintered for 25 minutes. Therefore the 20 minute samples in this experiment were used to determine all of the cooling rates. Longer sintering times allow alloying elements more time to diffuse, increasing the amount of martensite in the microstructure.

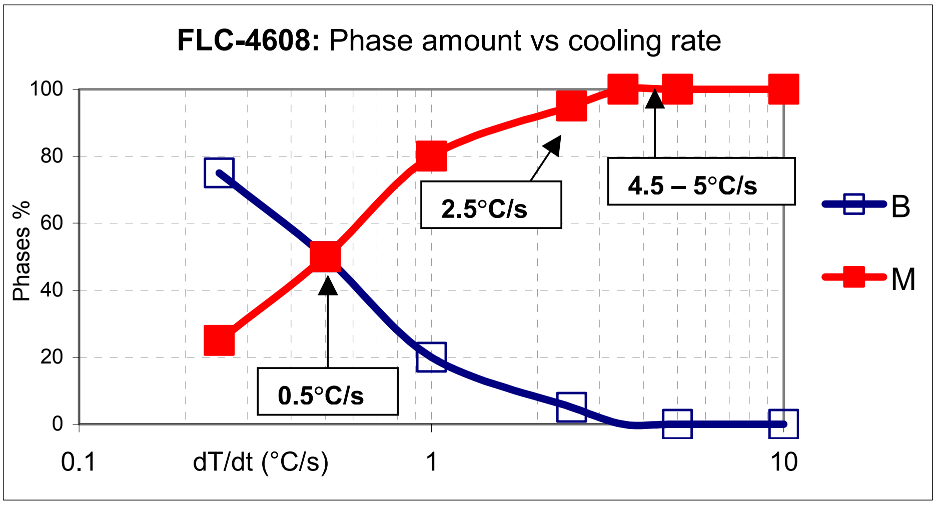

Figure 1. Effect of cooling rate on the microstructure of FLC-4608 with 0.7% C sintered for 25 minutes.

It is also important to note that the cooling rate is not constant during the cooling cycle, even though the fan speed was constant. Comparing a typical furnace profile shown in figure 3 to the CCT diagram in figure 2 reveals that the cooling rate changes in the region of the bainite nose and the start of martensite formation. If the cooling rate slows between 300 and 200°C (572 and 392°F), bainite may form. All cooling rates given in this paper were calculated for the temperature range of 800°C to 300°C (1472 to 572°F).

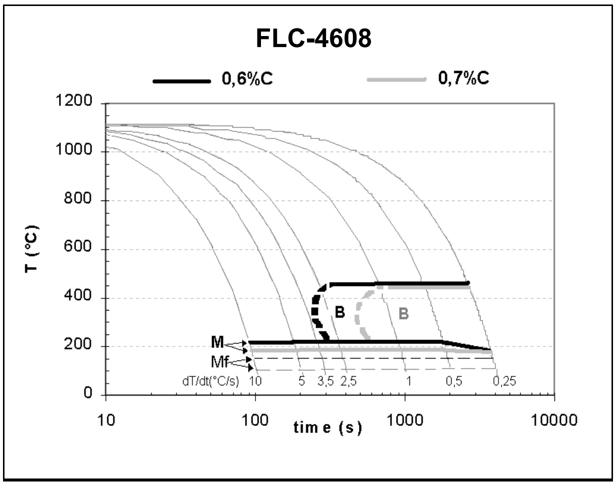

Figure 2. CCT diagram for FLC-4608

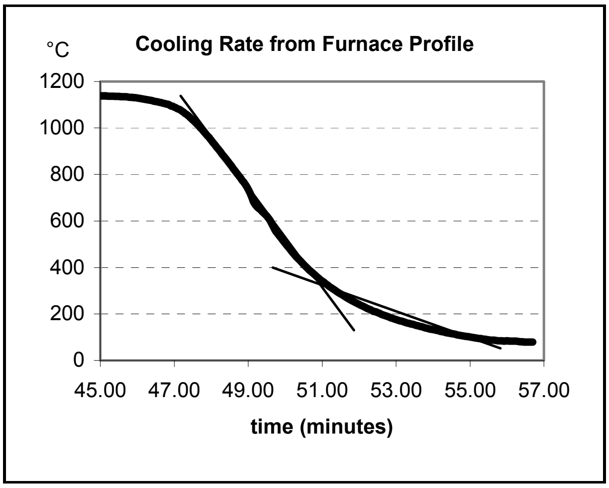

Figure 3. The cooling rate varies during cooling, so a temperature range must be specified when describing a cooling rate.

RESULTS AND DISCUSSION

Hardness and Mechanical properties

In general, increasing the sintering time and increasing the cooling rate increased the hardness and the strength of the materials. Figure 1 shows the hardness for all materials and conditions.

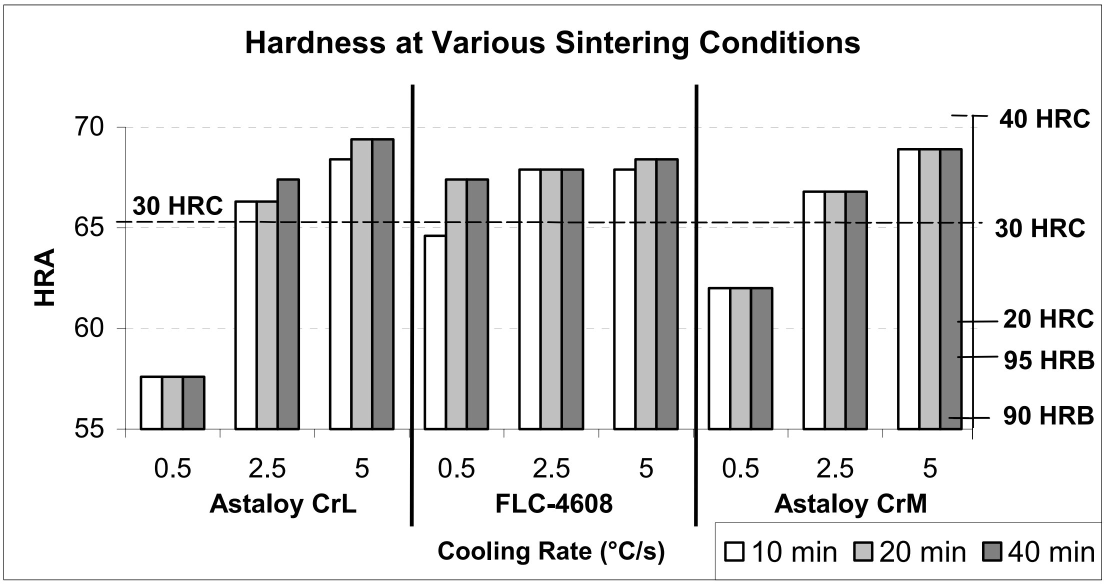

Figure 4. In general, hardness increased with sintering time and cooling rate.

The highest hardness was achieved with the CrL mix at the highest cooling rate (5.0 °C/s) after 20 or 40 minutes of sintering.

Because of its high alloying content, the FLC-4608 mix sinter hardened even without accelerated cooling. Increasing the cooling rate resulted in only slight hardness increases. However, although both the martensite content and hardness were high, tensile strength remained low unless accelerated cooling was used (Figure 5). The FLC-4608 mix (as well as the other mixes) achieved both high tensile strength as well as high hardness when accelerated cooling was combined with adequate sintering time.

Increasing sintering time above 20 minutes did not significantly improve hardness for the FLC-4608 or CrL. Twenty minutes may allow the alloying elements sufficient time to diffuse into the iron particle, transforming more austenite to martensite instead of bainite during cooling.

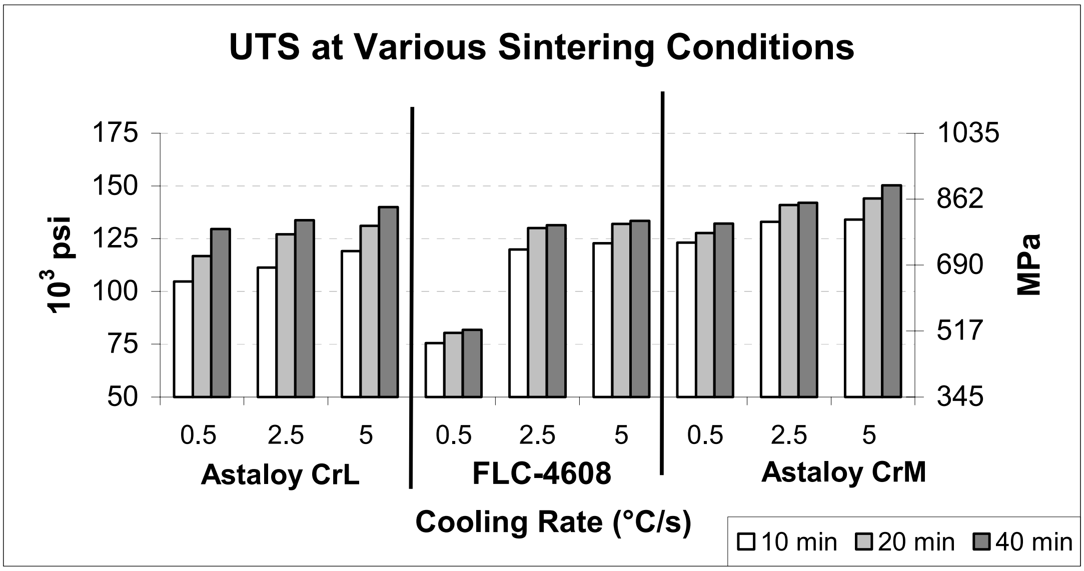

Figure 5. Ultimate Tensile Strength at various sintering conditions

The highest tensile strengths were obtained with the CrM mix at the longest sintering times and highest cooling rates.

Figure 6 shows that while hardness had a low dependence on sintering time, tensile strength improved dramatically with 20 minutes rather than 10 minutes of sintering. Allowing sufficient sintering time when sinter hardening is critical to achieve optimal mechanical properties. It is important to remember that high hardness may not necessarily indicate that the tensile strength is also high if the degree of sinter is poor.

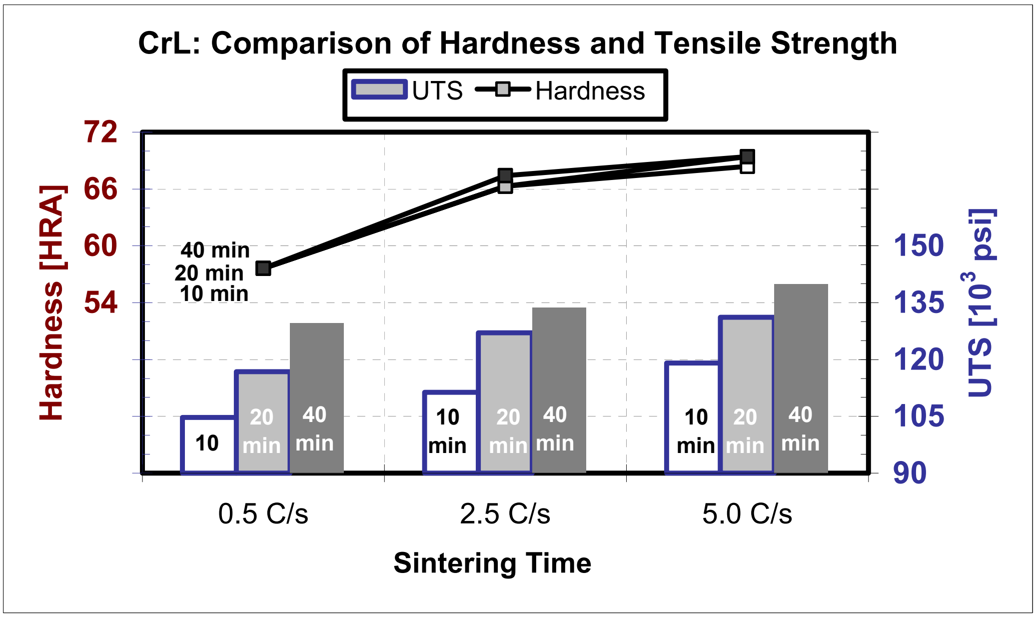

Figure 6. Sinter hardening produces high hardness even at short sintering times, but strength is much lower at the short sintering times.

Figure 7 shows that without sinter hardening, the tensile strength of FLC-4608 was low. When accelerated cooling was used, high tensile strengths were obtained. The low tensile strength of samples that received normal cooling may be due to the greater amount of bainite in the microstructure.

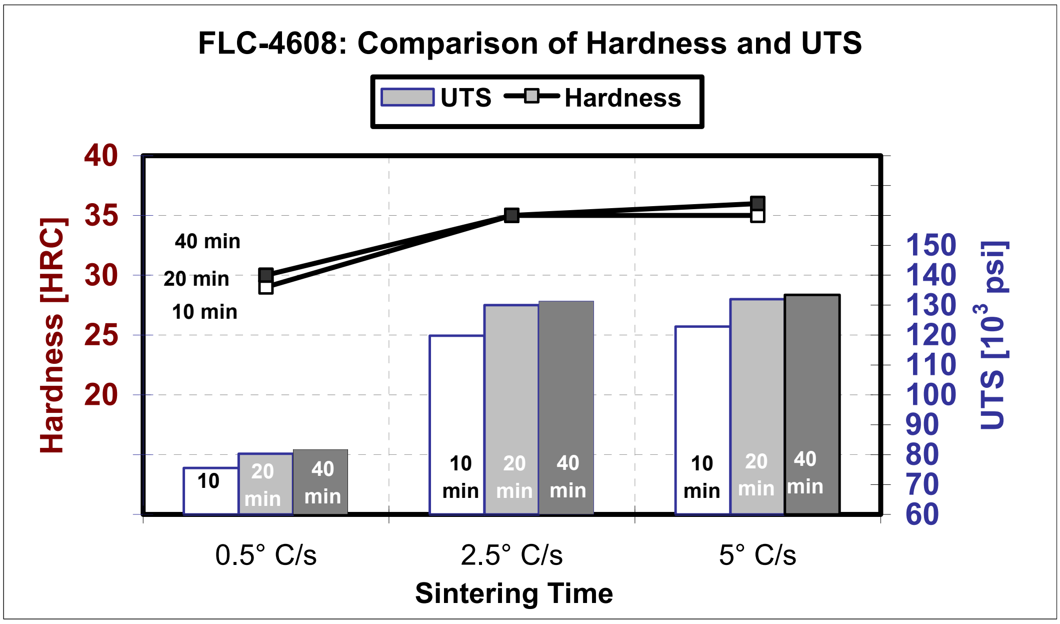

Figure 7. FLC-4608 attained much lower tensile strengths when normal cooling was used instead of sinter hardening, possibly because of the amount of bainite in the microstructure.

Similar trends occurred with transverse rupture strength, as shown in Figure 8.

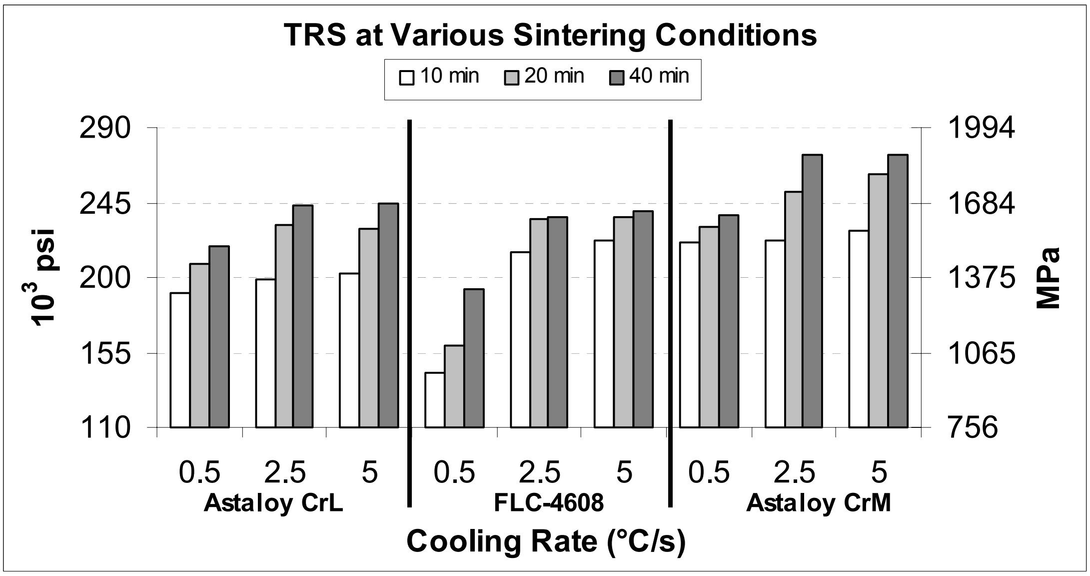

Figure 8. Transverse Rupture Strength at various sintering conditions

Density and dimensional change

Mechanical properties are heavily dependent on density. The mixes in this investigation were all compacted to a green density of 7.0 g/cm^3. However, the copper containing materials (Astaloy CrL + 1% Cu and the FLC-4608) experienced growth during sintering, while the third mix containing only Cr/Mo shrank, as shown in Figure 9. As a result, the copper-containing materials decreased in density during sintering, while the Astaloy CrM increased in density.

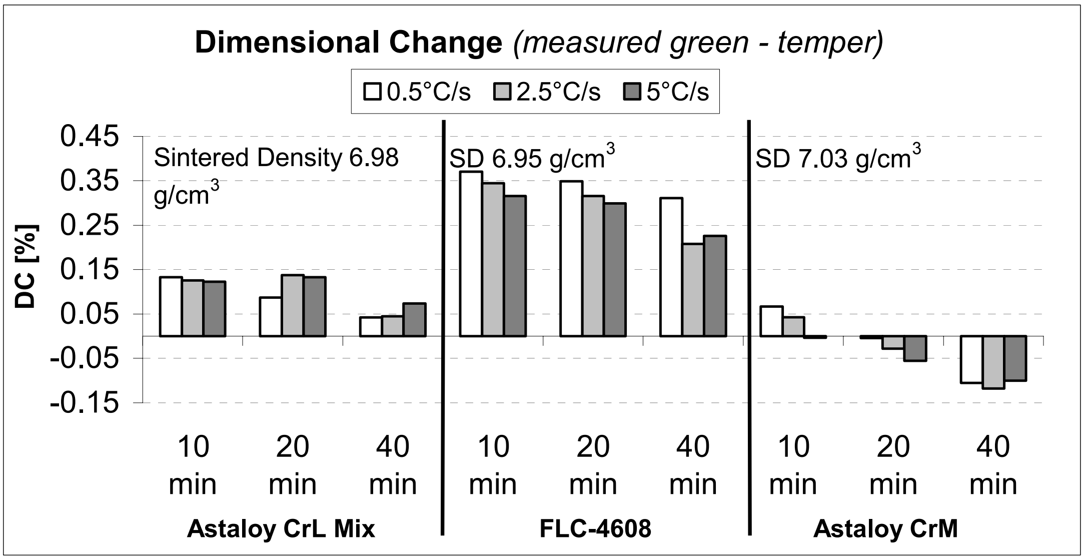

Figure 9. Dimensional change (measured from green state to tempered state) after various sintering conditions

Metallography

Materials that were sintered for only 10 minutes had poorly developed sintering necks. Prior particle boundaries are also present. Figure 10 contrasts the appearance of short and long sintering times on FLC-4608.

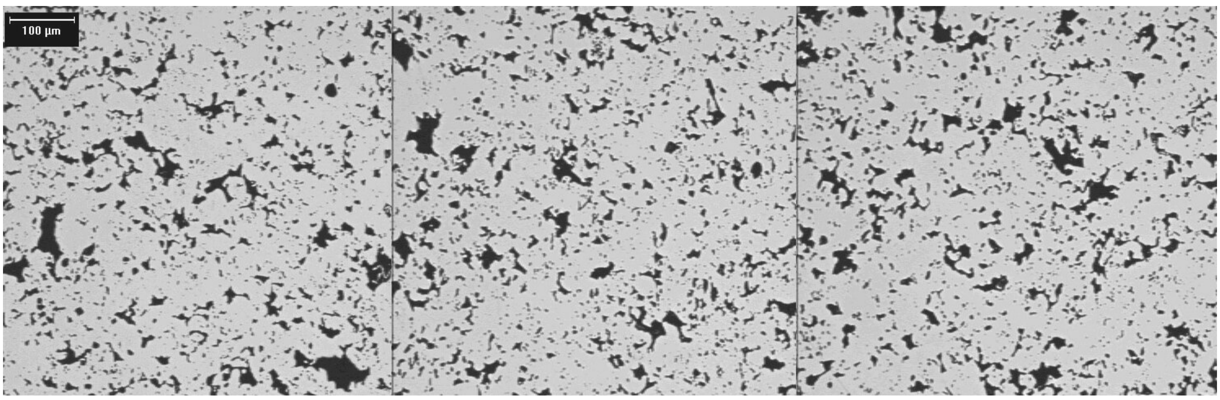

Figure 10a: FLC-4608, 10 min sinter. Incomplete sintering necks and prior particle boundaries are visible.

Figure 10b: FLC-4608, 20 min

Figure 10c: FLC-4608, 40 min. Pores appear rounded.

Tables VI - VIII show the phase analysis for the microstructures of the three materials.

Table VI: Phase analysis for FLC-4608.

Sintering time (minutes)	Cooling Rate (°C/s)	C as-sint (%)	Martensite (%)	Bainite (%)
10	0.5	0.67	71	29
20	0.5	0.66	73	27
40	0.5	0.66	74	26
10	2.5	0.66	94	6
20	2.5	0.62	98	2
40	2.5	0.66	99	1
10	4.5 – 5.0	0.67	99+	<1
20	4.5 – 5.0	0.66	100	0
40	4.5 – 5.0	0.67	100	0

Because of its high alloying content, the FLC-4608 mix sinter hardened even at normal cooling rates. Although both the martensite content and hardness were high without accelerated cooling, the tensile strength was low. Accelerated cooling produced high tensile strengths as well as high hardness.
Again, copper was concentrated in the grain boundaries of the bars sintered for 10 minutes, indicating that it had insufficient time to diffuse, and the amount of martensite increased with increased sintering time.

Table VII: Phase analysis for the CrL.

Sintering time (minutes)	Cooling Rate (°C/s)	C as-sint (%)	Martensite (%)	Bainite (%)
10	0.5	0.67	35	60
20	0.5	0.66	45	55
40	0.5	0.66	60	40
10	2.5	0.66	75	25
20	2.5	0.62	85	15
40	2.5	0.66	88	12
10	4.5 – 5.0	0.67	90	7
20	4.5 – 5.0	0.66	93	7
40	4.5 – 5.0	0.67	95	5

Figure 11 shows that 10 minutes of sintering is insufficient time for the copper to diffuse into the iron particles. Copper appears concentrated in the grain boundaries of the bars sintered for 10 minutes. Also note that the amount of martensite increased with increased sintering time, due to greater diffusion of alloying elements into the iron particles.

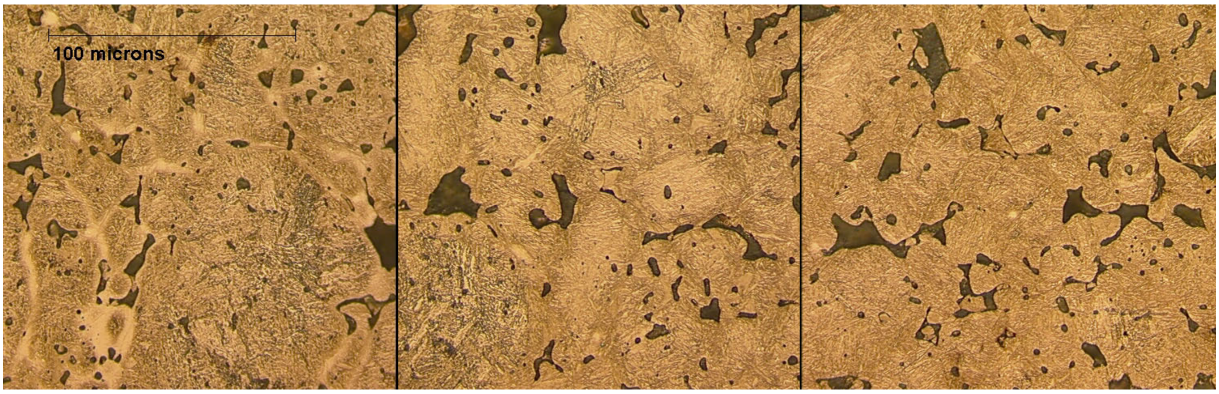

Figure 11a: CrL, sintered 10 min, 2.5°C/s cooling. Copper is concentrated in the grain boundaries.

Figure 11b: CrL Mix, 20 min sinter, 2.5 °C/s cooling

Figure 11c: CrL Mix, 40 min sinter, 2.5 °C/s cooling. Microstructure is mostly martensite.

Table VIII: Phase analysis for the CrM Mix

Sintering time (minutes)	Cooling Rate (°C/s)	C as-sint (%)	M (%)	B (%)
10	0.5	0.48	25	70
20	0.5	0.46	30	70
40	0.5	0.43	30	70
10	2.5	0.47	94	4
20	2.5	0.44	96	4
40	2.5	0.43	99	1
10	4.5 – 5.0	0.46	100	0
20	4.5 – 5.0	0.45	100	0
40	4.5 – 5.0	0.42	100	0

The CrM mix displayed the most striking shift from a primarily bainitic microstructure at normal cooling rates to a primarily martensitic structure when sinter hardening.

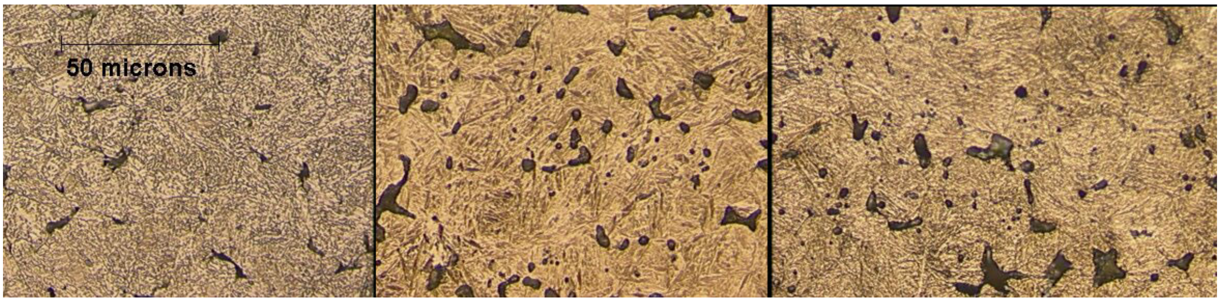

Figure 12a: Mostly bainitic structure of CrM sintered 40 min, followed by normal cooling.

Figure 12b: CrM, 20 min, 2.5 °C/s

Figure 12c: Martensitic microstructure of CrM sintered 40 min, 5.0°C/s

CONCLUSIONS

For a given alloy, controlling the cooling rate and sintering time determines the mechanical properties by producing the corresponding microstructure.

Although materials sintered for 10 minutes reached high hardness levels with the higher cooling rates, a sintering time of 20 minutes dramatically increased tensile strengths. Sintering for 40 minutes instead of 20 did not provide significant strength increases.

High hardness may not indicate high tensile strength or transverse rupture strength when the sintering time is short.

Cooling rates at a given set of furnace conditions must be experimentally determined for individual furnaces. Many factors influence cooling rate, including the fan speed, belt speed, load, and atmosphere flow rate and composition. Several trials may be necessary to determine optimum conditions for sinter hardening.

Chromium has a powerful effect on material hardenability.

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[3] Larsson, Mats, et al. "Properties of Cr-alloyed PM Materials." Presented at PTECH2003 Fourth International Latin Conference on Powder Technology in Guarujá, São Paulo, Brazil on November 20, 2003.
[4] Engström, Ulf. "Evaluation of Sinter Hardening of Different PM Materials." Presented at PM^2TEC 2000 in New York on May 31, 2000.

APPENDIX. SUMMARY OF TEST RESULTS

Grade	Cooling Rate (°C/s)	Sintering Time (minutes)	C-tot (%)	Sintered Density (g/cm³)	DC *(green-temper)* (%)	DC *(die-temper)* (%)	Hardness (HRC)	TRS [ksi]	TRS [MPa]	UTS [ksi]	UTS [MPa]
Astaloy CrL + 1% Cu + 0.75% C	0.5	10	0.67	6.97	0.13	0.24	94 HRB	191	1318	105	722
	0.5	20	0.66	6.98	0.09	0.20	94 HRB	208	1433	117	805
	0.5	40	0.66	6.99	0.04	0.15	94 HRB	219	1510	130	894
	2.5	10	0.66	6.97	0.13	0.24	32	199	1370	111	768
	2.5	20	0.62	6.97	0.14	0.25	32	231	1593	127	876
	2.5	40	0.66	6.97	0.05	0.16	34	243	1687	134	922
	5.0	10	0.67	7.00	0.12	0.23	36	202	1394	119	821
	5.0	20	0.66	6.99	0.13	0.24	38	230	1584	131	904
	5.0	40	0.67	7.00	0.07	0.18	38	245	1657	140	965
Astaloy A + 2% Cu + 0.8%C	0.5	10	0.74	6.94	0.37	0.48	29	142	982	76	521
	0.5	20	0.73	6.95	0.35	0.46	30	159	1096	80	554
	0.5	40	0.72	6.94	0.31	0.43	30	193	1332	82	564
	2.5	10	0.76	6.95	0.35	0.46	35	216	1487	120	826
	2.5	20	0.74	6.95	0.32	0.43	35	235	1620	130	906
	2.5	40	0.76	6.96	0.21	0.32	35	236	1627	131	906
	5.0	10	0.75	6.94	0.32	0.43	35	223	1535	123	847
	5.0	20	0.76	6.95	0.30	0.41	36	236	1555	132	904
	5.0	40	0.75	6.95	0.23	0.34	36	240	1656	133	920
Astaloy CrM +0.5%C	0.5	10	0.48	7.02	0.07	0.19	23	222	1528	123	849
	0.5	20	0.46	7.03	0.00	0.12	23	231	1592	128	880
	0.5	40	0.43	7.04	-0.11	0.02	23	238	1639	132	911
	2.5	10	0.47	7.04	0.04	0.17	33	223	1535	133	917
	2.5	20	0.44	7.03	-0.03	0.10	33	252	1737	141	977
	2.5	40	0.43	7.04	-0.12	0.01	34	273	1885	142	971
	5.0	10	0.46	7.03	0.00	0.12	36	228	1572	134	924
	5.0	20	0.45	7.03	-0.06	0.07	37	262	1804	144	975
	5.0	40	0.42	7.04	-0.10	0.03	37	274	1888	150	1036