Influence of Cooling Rate on the Microstructure and Mechanical Properties of Different Low Alloy PM Materials

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Abstract

Sinter hardening is an established cost-effective process for producing high strength parts that combines sintering and accelerated cooling in one sintering cycle, and also removes the need for additional heat treatment. It is known that the cooling rate after sintering greatly influences the microstructure of PM steel through the formation of martensite, which strongly determines its final properties. Alloying elements such as molybdenum, chromium, nickel and copper all promote hardenability. By increasing the hardenability of the material, martensite can also be obtained at lower cooling rates.

In this study, a number of materials used for sinter hardening (Mo/Cu hybrid low alloy steel and Cr/(Mo) pre-alloyed low alloy steels) have been investigated utilizing various sintering temperatures and cooling rates in a new pusher/roller furnace. The mechanical properties and microstructures achieved for each individual PM material are described. By understanding how sintering temperatures and cooling rates influence microstructure and mechanical properties, it is possible to optimize the sintering cycle for each material and its applications.

Keywords: Sinter-hardening, Cooling rate, Mechanical property, Microstructure

Introduction

As a cost-effective process, sinter hardening has been applied more and more in the PM industry to manufacture high performance components. This has been achieved through utilizing alloying elements with high hardenability such as molybdenum, chromium, nickel and copper in combination with an accelerated cooling rate [1-4]. When sinter hardening, the type and amount of alloying element, sintering temperature and time, and cooling rate after sintering, all affect microstructures [5-7] and influence the resulting properties.

Increasing the cooling rate can transform more austenite into martensite which is beneficial for hardness and strength. The sintering temperature can promote better sintering necks, rounder pores and alloying diffusion, but also grain growth which is detrimental to mechanical properties [8]. To better understand the interaction of cooling rates and sintering temperatures upon mechanical properties and microstructures, three sinter-hardenable PM materials were evaluated at different sintering temperatures and cooling rates. The mixes were based on an MPIF sinter-hardening grade, which contains Cr, Mo and Cu.

Experiments

Material

Three different powder mixes were prepared and Distaloy DH, Astaloy CrM and Astaloy CrA were used as base powders. Cr materials have been investigated in many studies for decades, but not Astaloy CrA with a low Cr content under a high sintering temperature [9-15]. 1 wt.% -200 mesh electrolytic copper powder and natural graphite (C-UF4) are added for common sinter hardening applications. The chemical

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composition, identification codes and total alloy content of the mixes are presented in Table Ⅰ. Hardenability multiplying factors of the mixes were calculated according to the formula: $(1+0.24\times\%C)\times(1+0.27\times\%Cu)\times(1+0.52\times\%Ni)\times(1+3.14\times\%Mo)\times(1+4.1\times\%Mn)\times(1+2.33\times\%Cr)$ [16]. It can be seen that the CrM mix has the highest hardenability while the CrA1Cu mix has the lowest. However, for the DH and CrA1Cu mixes, Cu was not pre-alloyed so the multiplying factors were not directly transferable due to alloying diffusion during sintering.

Table 1. The chemical composition and identification codes of the three mixes.

Mix No.	MPIF grade	Identification code	Composition %					Total metallic alloy %	Hardenability Multiplying factors
			Fe	**Cu**	**Mo**	**Cr**	**C**		
1	FLC4908	DH	Bal.	2**	1.5*	-	0.6	3.50	10.1
2	FL5305	CrM	Bal.	-	0.5*	3*	0.45	3.50	22.8
3	FL5108-Cu	CrA1Cu	Bal.	1	-	1.8*	0.6	2.8	7.5

*prealloy **diffusion bonded

Sample preparation

Tensile strength test specimens (ISO 2740) and impact energy test specimens (MPIF60) were compacted to green density@7.0g/cc.

Processing condition

All the tensile strength and impact energy test specimens were compacted using conventional methods. The sintering was carried out at 1120 ℃ and 1250 ℃ for 30 minutes in N_2/H_2=90/10 in a newly designed industrial size pusher/roller furnace with an accelerated cooling system. The newly designed furnace has a pusher system for dewaxing and a roller system for sintering and cooling. By setting the cooling fan rotation frequency to 5 Hz, 15 Hz and 25 Hz, three different cooling rates, 0.5-1.5 ℃/s, 2.5-3.5 ℃/s, 4-5 ℃/s were achieved on the test bars as can be seen in Figure 1. Afterwards, tempering was carried out at 200 ℃ for 1h in air.

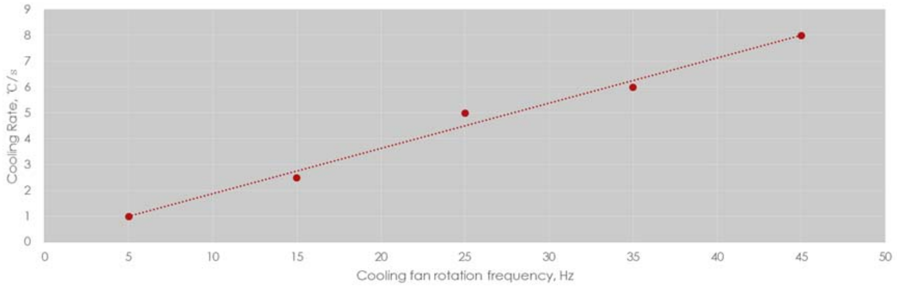


Fig. 1. The relationship of cooling fan rotation frequency and nominal cooling rate for the furnace.

Test

Sintered density (ISO 2738), tensile strength (ISO 6892-1), impact energy (MPIF40) and macro hardness (ISO 4498) were tested. Apparent hardness was performed on both upper (highest distance from belt) and bottom (close to belt) surfaces. Dimension change was tested on tensile test bars with length direction (as tempered to green).

Metallography

Tensile test specimens were prepared using cross sections for metallographic investigation. Photomicrographs were taken of the microstructures after etching using a mix of 1-2 % Nital and Picral.

The amount of pealite, martensite and bainite was determined by image analysis (ASTM E562).

Result and discussion

Mechanical properties

The sintered density, carbon and oxygen contents influenced by the sintering temperatures are listed in Table Ⅱ. Higher sintering temperature will result in component shrinkage and thus higher density, more oxide reduction and more carbon loss for the materials in a N2/H2 atmosphere. From the table it can be seen that density increased 0.01-0.07 g/cm^3, carbon decreased 0.05-0.08 wt.%, and oxygen decreased up to 0-0.04 wt.% at 1250 ℃ compared to1120 ℃ sintering. The oxygen content for materials containing Cr at 1250 ℃ was relatively low at 0.01 wt.%.

Table Ⅱ. Sintered density, carbon and oxygen contents of specimens sintered at different temperatures.

Identification Code	**As sintered density g/cm^3**		**As sintered Carbon Wt.%**		**As sintered Oxygen Wt.%**	
	1120℃	**1250℃**	**1120℃**	**1250℃**	**1120℃**	**1250℃**
DH	6.93	6.99	0.57	0.52	0.01	0.01
CrM	7.0	7.1	0.41	0.33	0.05	0.01
CrA1Cu	6.97	7.04	0.57	0.51	0.04	0.01

From Figure 2 it can be seen that increasing the sintering temperature from 1120 ℃ to 1250 ℃ did not improve hardness though sintered density improved. Hardness slightly decreased due to increased carbon loss and grain growth at a higher temperature sintering. The cooling rate contributed to improvements in hardness when it was increased from 0.5-1.5 ℃/s to 4-5 ℃/s, however, for DH and CrM the improvement is not pronounced when the cooling speed was higher than 2.5 ℃/s. The macro hardness achieved 32-34 HRC for DH, 33-37 HRC for CrM, and 31-37 HRC for CrA1Cu at a common sinter hardening cooling speed higher than 2.5 ℃/s. For CrA1Cu, the macro hardness was slightly higher than the other two materials at a cooling rate of 4-5 ℃/s for both sintering temperatures and showed 37 HRC. Due to increased carbon loss at high temperature sintering, a hardness drop was found at 1250 ℃ sintering for CrM. Less martensite but more bainite formed for DH due to more Cu diffusion from the boundaries into the center of particles at a high sintering temperature and a slow cooling rate of 0.5-1.5 ℃/s. This caused hardness to decrease which can be seen in the metallography images. However, at higher cooling rates there was little affect upon hardness, although even more Cu diffused at a high sintering temperature.

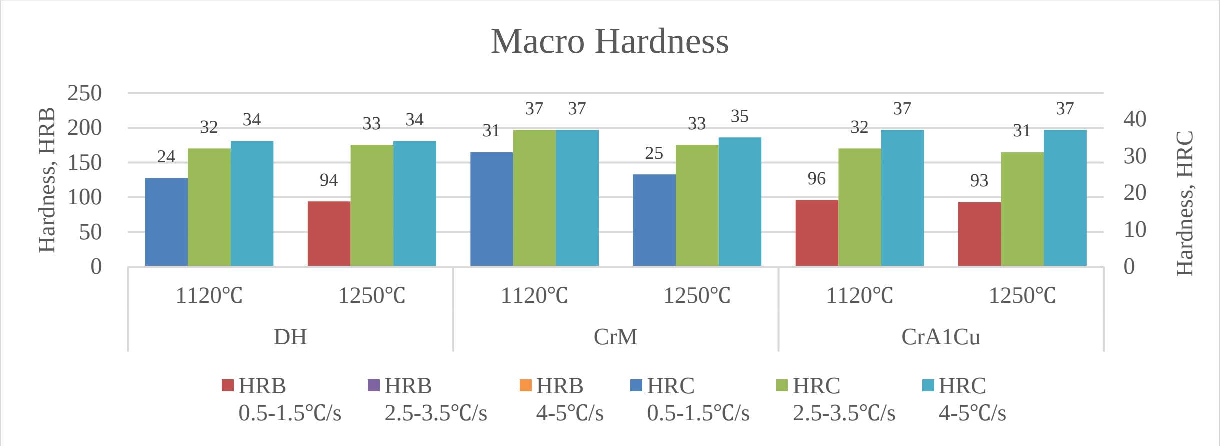


Figure 2. Macro hardness of specimens.

The tensile test results are shown in Figure 3, 4 and 5. From these it can be seen that the sintering temperature contributes greatly to yield strength and ultimate tensile strength at a slow cooling rate of 0.5-1.5 ℃/s. However, through better sintering necks and rounder pores it significantly increases UTS at a cooling rate higher than 2.5 ℃/s, as well as the elongation and impact energy for all the specimens. By increasing cooling speed from 0.5-1.5 ℃/s to 2.5-3.5 ℃/s, yield strength can increase 15~55 % and ultimate tensile strength can increase 10%~50 %. This is more pronounced at higher sintering temperatures. However, for UTS no improvements were observed when the cooling speed was higher than 4 ℃/s.

CrM got the highest UTS among the three materials when processed at the same condition. CrA1Cu has a lower alloying content and lower hardenability, thus its UTS was lower than the other two materials at cooling rates lower than 3.5 ℃/s using conventional sintering. However, when it was sintered at high temperatures its UTS was comparable with DH. The highest UTS for each individual material was obtained with a cooling rate higher than 2.5 ℃/s at 1250 ℃.

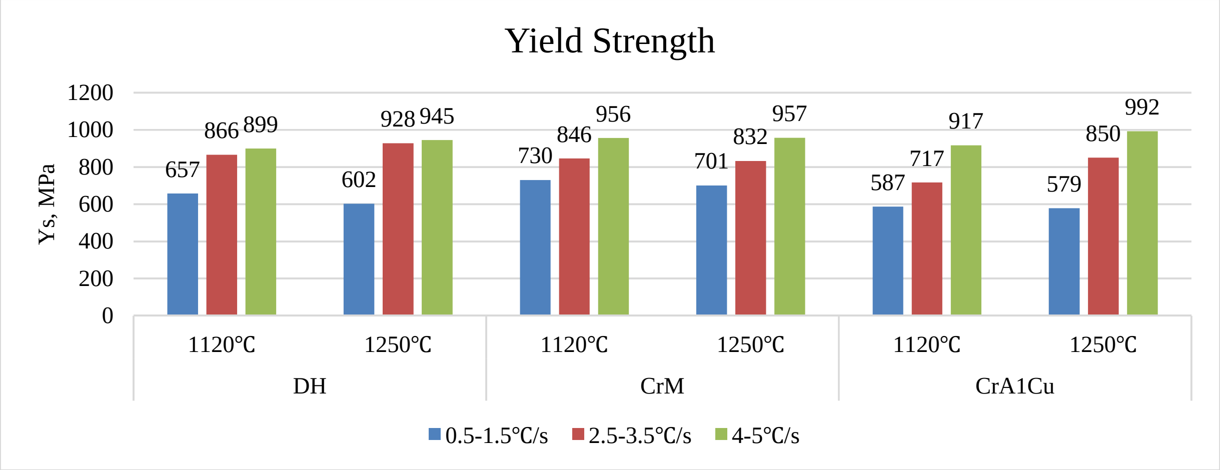


Figure 3. Yield strength of specimens.

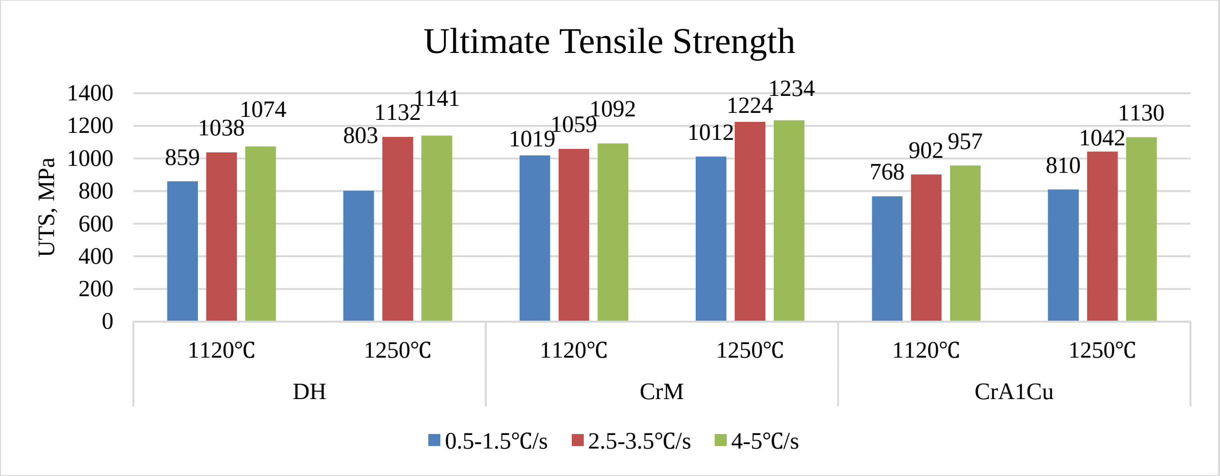


Figure 4. Ultimate tensile strength of specimens.

The largest increase in elongation for all the materials was obtained with a slow cooling rate of 0.5-1.5 ℃/s when sintering at 1250 ℃. With an increased cooling rate, more hard phase formed which increased UTS but reduced ductility, so therefore elongation generally decreased. At a slow cooling rate of 0.5-1.5 ℃/s, CrA1Cu has increased elongation when compared to CrM and DH.

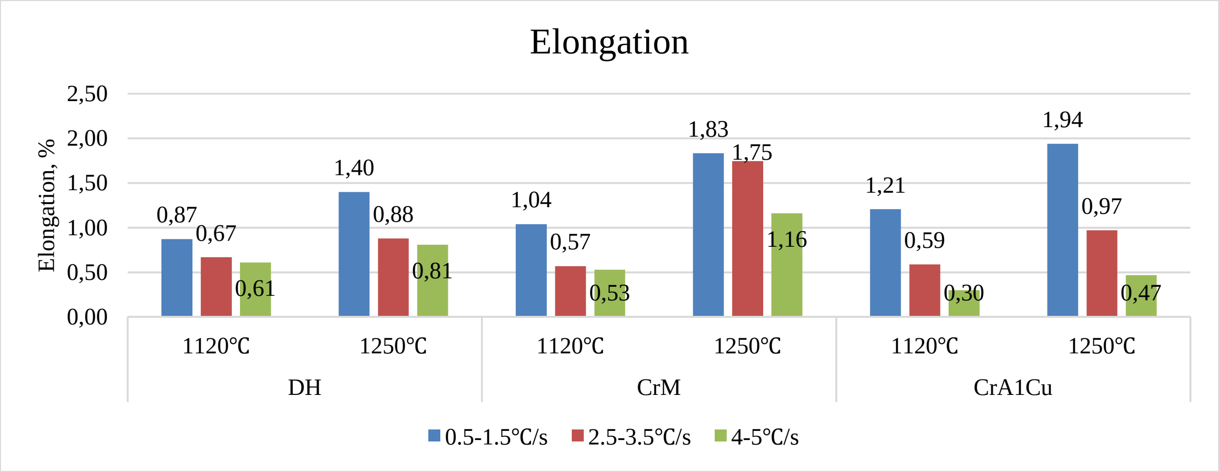


Figure 5. Elongation of specimens.

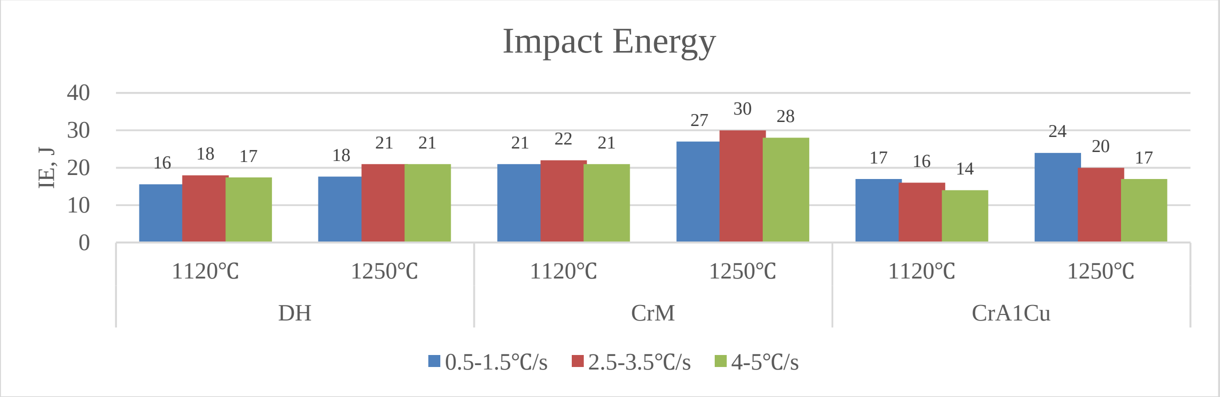
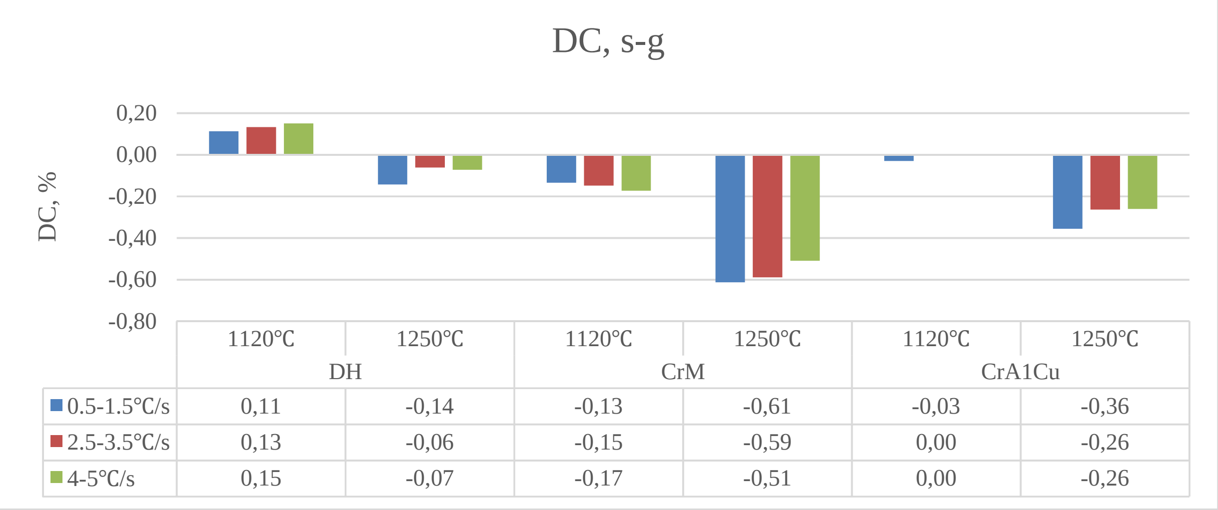


Figure 6. Impact Energy of Specimens under different cooling speeds.

The impact energy was listed in Figure 6. The highest impact energy of DH and CrM appeared at a cooling rate of 2.5-3.5 ℃/s and sintering at 1250 ℃. Here you can see this value has increased and then decreased with an increase in cooling rate. However, for CrA1Cu, the highest impact energy appeared at a slower cooling rate of 0.5-1.5 ℃/s under 1250 ℃ and decreased with higher cooling rates. Similar to elongation, at a slow cooling rate of 0.5-1.5 ℃/s, the impact energy of CrA1Cu is higher than DH.

Dimensional change

The mixes in the investigation were all compacted to a green density of 7.0 g/cm^3. DC from tempered to green is presented in Figure 7.



	1120℃	1250℃	1120℃	1250℃	1120℃	1250℃
	DH		CrM		CrA1Cu	
🟦 0.5-1.5℃/s	0,11	-0,14	-0,13	-0,61	-0,03	-0,36
🟥 2.5-3.5℃/s	0,13	-0,06	-0,15	-0,59	0,00	-0,26
🟩 4-5℃/s	0,15	-0,07	-0,17	-0,51	0,00	-0,26

Figure 7. Dimensional change for tempered green TS specimens.

The dimension for DH containing 2 wt.%Cu experienced growth during sintering at 1120 ℃, while the other materials shrank. For CrA1Cu at 1120℃ sintering, there was zero dimension change from green to tempered. With an increased sintering temperature, all the materials shrank due to more volume diffusion. As a result, at 1120 ℃ sintering, DH decreased in density while other materials increased in density. As the cooling rate increased, slightly more swelling could be found due to more martensite formation with bigger volumes.

Metallography

For all the materials, an increased sintering temperature resulted in less oxide, better sintering necks and rounder pores, which were beneficial to strength and toughness.

An optimal microstructure for a sinter-hardened material would show more than 90% martensite at the surface of the part with no less than 70% martensite in the core. This structure would provide the surface hardness and toughness of a quenched microstructure without the high stress resulting from accelerated cooling. Therefore, it is important to know the cooling rate and alloy content that provide the required hardenability for a part of a given mass and density[7]. To compare the material's hardenability, martensite amounts at different cooling rates were investigated and presented in Figure 8. In general, the martensite amount increased with higher cooling rates. To get more than 90% martensite, CrA1Cu and DH needed a cooling rate of 4-5 ℃/s, while CrM needed 2.5-3.5 ℃/s. The martensite amount differed somewhat in relation to sintering temperatures. Normally more martensite could be found at 1120 ℃ which could be due to less carbon loss. In addition, element diffusion influences the hardenability of the materials in micro areas, whilst different austenite grain sizes influence martensite formation at various sintering temperatures.

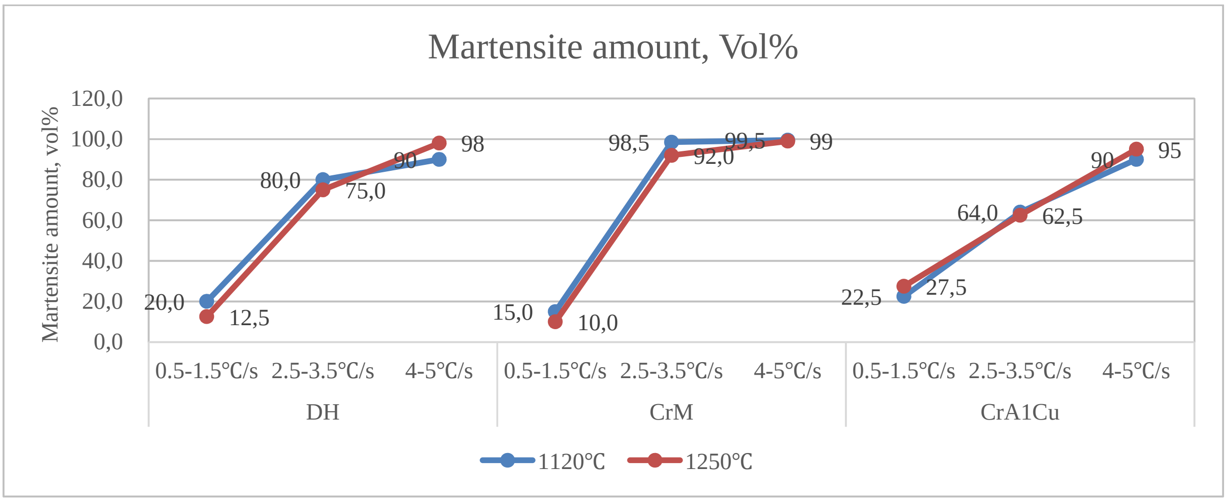
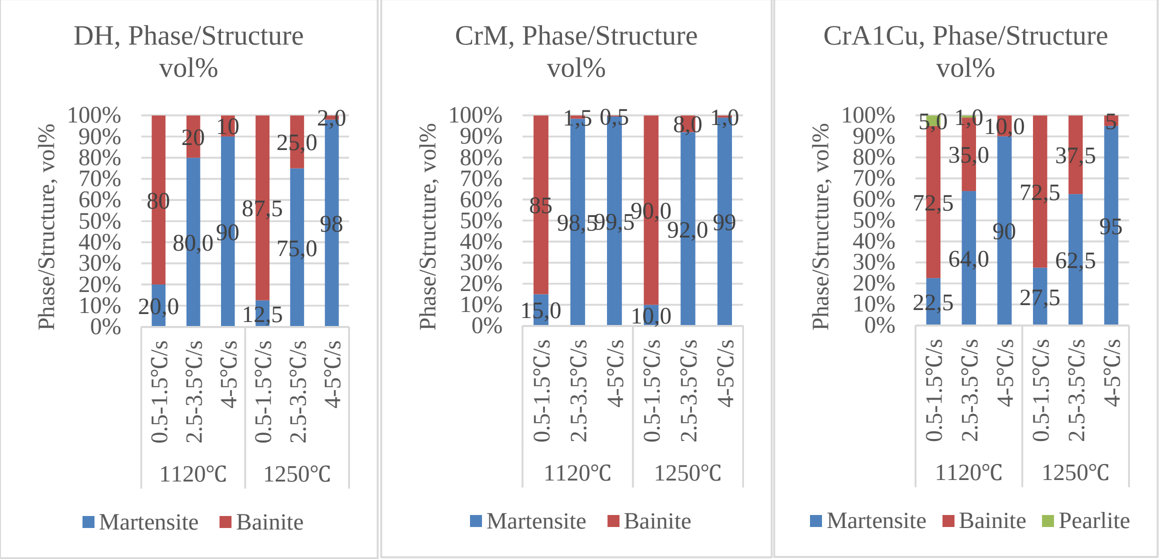


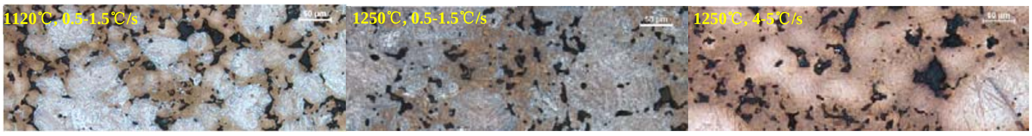
Figure 8. Martensite amount of TS specimens.

In Figure 9 you can see the phase/structures amount in each individual material under different conditions, and in Figure 10 the microstructures for the typical processing of each material are presented. The dominant phases for the materials were martensite and bainite, while for CrA1Cu some pearlite could be found under slow cooling rates. As cooling rates increased, pearlite/bainite decreased and martensite increased. The dark-brownish network at the particle boundaries is diffused copper showing a copper concentration gradient in materials with added Cu. As seen from figure 10 (a), copper diffusion was wider and had less color contrast at a higher sintering temperature. This means the Cu distributed more evenly, so a lower Cu content at Cu-rich area, but more Cu content at a Cu-lean area. Lower Cu content at a Cu-rich area led to less retained austenite and also reduced the material hardenability with less martensite. Higher Cu content at a Cu-lean area led to higher hardenability and more bainite thus influencing the mechanical properties.

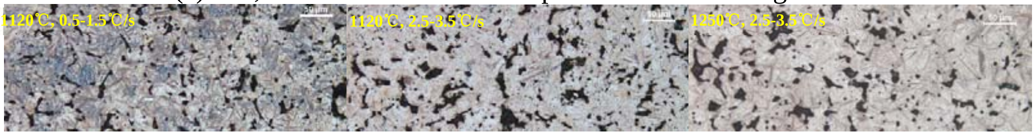


(a) (b) (c)

Figure 9**.** Phase amounts for TS specimens.



(a) DH, sintered at different temperatures and cooling rates.



(b) CrM, sintered at different temperatures and cooling rates.

(c) CrA1Cu, sintered at different temperatures and cooling rates.

Figure 10. Microstructure of TS specimens for materials and typical processing.

Cconclusions

Mechanical properties and microstructures were investigated for three MPIF standard sinter hardening materials at 7.0 g/cm^3 under different sintering temperatures and cooling rates in a pusher/roller furnace.

1. Generally, a higher cooling rate obtained more amounts of martensite resulting in greater hardness and strength. However, when the cooling rate was higher than 4 ℃/s there was no significant improvement in strength for all materials, and on hardness for DH and CrM. A higher sintering temperature could increase the strength for the materials when the cooling rate was higher than 2.5 ℃/s. Moreover, high temperature sintering promoted greater elongation and impacted upon energy results through improved sintering necks and rounder pores.
2. With dimensional change, the cooling rate caused slight component swelling, so was not significant. A high sintering temperature resulted in significant dimension shrinkage.
3. Astaloy CrM has the highest hardenability and strength in all the materials with a carbon content of 0.3-0.45 wt.%. Under the conditions tested, a high hardness of 37 HRC and a strength of 1224 MPa was achieved at a 2.5-3.5 ℃/s cooling rate under 1250 ℃. A higher carbon content should be considered if a higher hardness is required.
4. The optimal conditions for achieving robustness and maintaining toughness of Distaloy DH with 0.6% C was 1250 ℃ sintering and a 2.5-3.5 ℃/s cooling rate. Lower hardness and strength was achieved at a high sintering temperature and slow cooling rate due to greater Cu diffusion affecting hardenability in local areas. An increased cooling rate and a high sintering temperature were major factors in producing a stronger material.
5. The hardness for Astaloy CrA with 1 wt.%Cu was higher at a cooling rate of 4-5 ℃/s with an almost fully martensitic structure especially under high temperature sintering. This was due to the addition of more carbon compared with the other two materials. To increase strength and hardness a high cooling rate is needed but this results in less toughness. If further strength improvements are needed, a lower carbon content may help. With high carbon content a high cooling rate can reduce the martensite brittleness.

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