Journal of Achievements in Materials and Manufacturing Engineering
VOLUME 37
ISSUE 1
November
2009

Influence of cooling rates on properties of pre-alloyed PM materials

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Received 22.08.2009; published in revised form 01.11.2009

Properties

ABSTRACT

Purpose: The paper focuses on microstructural and mechanical properties of pre-alloyed Astaloy CrL and CrM sintered steels with high addition of carbon.
Design/methodology/approach: The main objective of the present work was to establish the effect of cooling rates on the microstructure and properties such as: Charpy impact test, microhardness, wear resistance (disk on disk test) were evaluated depending on chemical composition. Compacts containing low amounts of chromium, molybdenum and high amount of graphite were sintered in a vacuum furnace at 1120ºC in vacuum atmosphere and rapidly cooled in nitrogen with two different rates. Then compacts were tempered in vacuum, and cooled in nitrogen. Obtained samples were analysed by light optical microscopy (LOM) for microstructure observation and scanning electron microscopy (SEM) with EDS for chemical composition.
Findings: Sinter hardening is a cost-effective process that consists of sintering and heat treatment in one step, so it minimizes the number of processing steps. It is known that the cooling rate following sintering greatly affect material microstructure, which determine the final properties of sinter-hardened materials. The objective was to understand how sintering conditions influence the development of microstructures and thereby control mechanical properties of materials.
Practical implications: Changing the amount of graphite element and cooling rates, will affect the amount of ferrite, perlite, martensite and bainite in the microstructure. Further tests should be carried out in order to examine different cooling rates.
Originality/value: Sinter-hardening of CrL and CrM pre-alloyed powders with addition of graphite was investigated to study cooling mechanism.
Keywords: Powder metallurgy; Sintering; Sinter-hardening

Reference to this paper should be given in the following way:
L.A. Dobrzański, M. Musztyfaga, Influence of cooling rates on properties of pre-alloyed PM materials, Journal of Achievements in Materials and Manufacturing Engineering 37/1 (2009) 28-35.

1. Introduction

Powder metallurgy is a continually and rapidly evolving technology covering mostly metallic and alloy materials, and a wide variety of shapes. PM includes the production of metals in powder form and a manufacture from such powders of useful objects by the process known as sintering. In many cases individual engineering components are produced directly by process such as components being referred to indiscriminately as sintered components, sintered parts or PM parts [1-3].

The production of sintered components represents the main groups for the application of powder metallurgy procedures. This trend expands powder metallurgy into new areas of technology and industry, so that powder metallurgy is becoming a part of technical and economic development. This is also a result of the fact that the properties of PM are equal to or in many cases even higher than those of convectional products [1-4]. Moreover, the complexity of PM lies in the interaction between three "ingredients" necessary to achieve a component. These "ingredients" are compaction, powder and sintering (Fig. 1). A high level of knowledge of the relation between these ingredients is of utmost importance for high strength components in order to fulfil requirements for quality and cost [5-7].

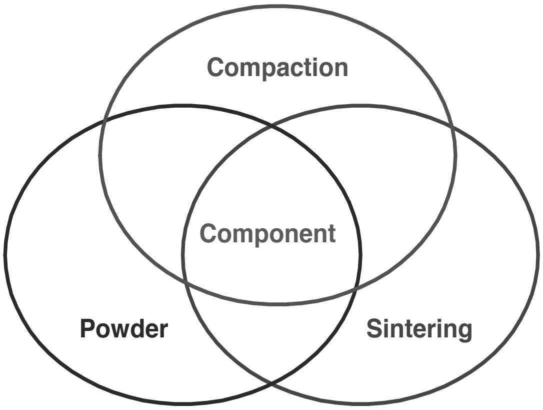


Fig. 1. Interaction between powder, compaction and sintering to fulfil component requirement [5, 6]

The properties of sintered parts and materials (chemical, physical, mechanical, toughness and special) are a result of the interaction of three parameters: powder properties, force (pressure) and heat (time, temperature) as physical quantities. While the chemical composition and certain processing properties of powders can be varied over a wide range, the use of pressure and heat is restricted to a certain extent because of technical reasons. The parameters controlling the quality of sintered parts are shown in Fig. 2. Taking into account some of the previously mentioned aspects, special attention will now be drawn to defining more accurately a number of general characteristics of powders and technology, with emphasis on their evaluation and application in production [1, 4].
Sinter-hardening is an increasingly popular technique, which offers an alternative method through hardening the powder metal components without the application of traditional austenitisation, quench and tempering cycle [8, 9]. Sinter hardening is a cost-effective process that combines sintering and heat treatment in a single cycle [10]. Sinter-hardening not only aims at productivity and property enhancement but also at economic feasibility [11-15]. The properties resulting from sinter-hardening are controlled by fundamental parameters such as: green density, convective cooling and cooling rate. These fundamental parameters are directly and indirectly controlled by the processing parameters such as: cooling rate, sintering time and others [16-19].

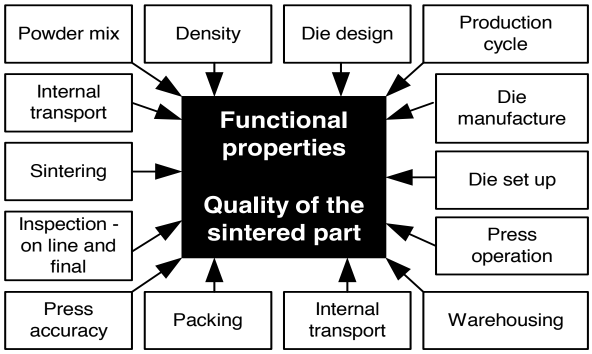


Fig. 2. Parameters controlling the properties of sintered parts and parameters which must be controlled [1]

Cooling rate is the most important processing parameter in relation to sinter-hardening. Control of the cooling rate is a function of several variables including thermal mass, powder composition (alloying elements), density, part geometry and a velocity of the fluid in the cooling section of the furnace. Many of the processing parameters affect the cooling rate in the part directly and indirectly. One way to increase the cooling rate is by increasing the proportion of nitrogen in the cooling section of the furnace during sinter-hardening. Nitrogen in the sintering atmosphere affects the cooling rate, providing a faster quench, increases apparent hardness and fraction of martensite. Control of cooling rate is essential for optimization of final microstructure and properties of steel [20].

Sintering temperature is a dominant factor in both densification and antiparticle neck growth. The effect of sintering temperature on sinter-hardening has been studied, so it has been reported that a higher sintering temperature promotes a more homogenous microstructure, which can improve the ability of steel to form martensite. Higher sintering temperature also result in higher impact properties. Sinter-hardening materials processed by warm compaction exhibit improved mechanical properties compared to those processed by cold compaction [20].

Sintering time. A longer time at peak temperature improves the mechanical properties. At longer sintering times there is more densification and shrinkage [20].

Green density increases not only hardness and strength values, but also ductility and impact properties increase dramatically. Green density science also effects final density, higher green densities will affect the local cooling rate and consequently the hardness of steel. Compaction pressure has an effect on green density. The density obtained after warm compaction is higher than that obtained after cold compaction. Additives such as lubricants effects density during the compaction phase. The role of lubricant is to reduce the friction force between the powder and tool walls, and also between the particles.

Just before the sintering process, the lubricant must be removed from the compact to avoid interfering with the formation and growth of bounds between the particles [20].

Sintered density has a significant effect on the thermal conductivity of a PM material (higher the sintered density, higher the thermal conductivity). While higher thermal conductivity has no effect on sinter-hardening of the surface of a PM part, therefore, the fraction of martensite formed. Tensile strength is directly related to the final density [20].

1.1. Effect of carbon, molybdenum and chromium

Carbon has a moderate tendency to segregate, and carbon segregation is often more significant than the segregation of other elements. Carbon, which has a major effect on steel properties, is the principal hardening element in all steels. Tensile strength in the as-rolled condition increases as carbon content increases. Ductility and weldability decrease while increasing carbon.

Molybdenum as an alloying element in steel decreases the critical cooling rate, because it suppresses the perlite transformation. It has a lower affinity for oxygen and is therefore proffered in sinter-hardening alloys Molybdenum is the third highest element in terms of increasing hardenability, after chromium and manganese.

Chromium is generally added to steel to increase resistance to corrosion and oxidation, to increase hardenability, to improve high-temperature strength, or to improve abrasion resistance in high-carbon compositions. Chromium is strong carbide former.

The processing parameters, when selected correctly, affect the fundamental parameters, which in turn affect the mechanical properties [20]. The aim of work was to increase the mechanical properties of experimental sintered materials, manufactured from Astaloy CrL and Astaloy CrM powders with a graphite additive in relation to commercial sintered materials manufactured from these powders. Introducing graphite performs a function as a lubricant during pressing a mixture of powders, decreases solidus temperature, what in many cases initiates a sintering process and increases hardenability sintered materials during rapid cooling directly from a temperature i.e. during a sinter-hardening process [20, 21].

2. Experimental procedure

There were used in researches following output powders such as (Fig.3):

- Astaloy CrL pre-alloyed powder is produced by Swedish Höganäs company,
- Astaloy CrM pre-alloyed powder is produced by Swedish Höganäs company,
- GR lamellar graphite powder is produces by Swedish Höganäs company.

Different compositions have been tested in order to investigate the influence of high carbon content and cooling rates on the microstructure and properties. The chemical composition of iron-base powders used in this study was for:

- Astaloy CrL (0.2%Mo, 1.5%Cr, <0.01%C, 0.16%0_2-tot);
- Astaloy CrM (0.5%Mo, 3%Cr, <0.01%C, 0.21%0_2-tot).

Next to the base powders are further mixed with graphite to obtain the desired strength in the materials and with lubricant to reduce the friction force between the powder and tool walls, and also between the particles. The amount of graphite which is mixed with the iron-base powder is 0.6% and lubricant is 0.75%. Qualitative and quantitative chemical composition of studied powder mixes is presented in Table 1. The metal powders and lubricant were mixed using a turbula mixer. From prepared powder mixtures with using a method of uniaxial pressing in die (die with free motion) were preformed three sets of samples: dog bone for bending test, rectangular (5 x 10 x 55) for Charpy test and disk (40 mm) diameter for wear test. The samples were obtained using 200 kN hydraulic press. Pressing was carried out with applied pressure 500 and 600 MPa.

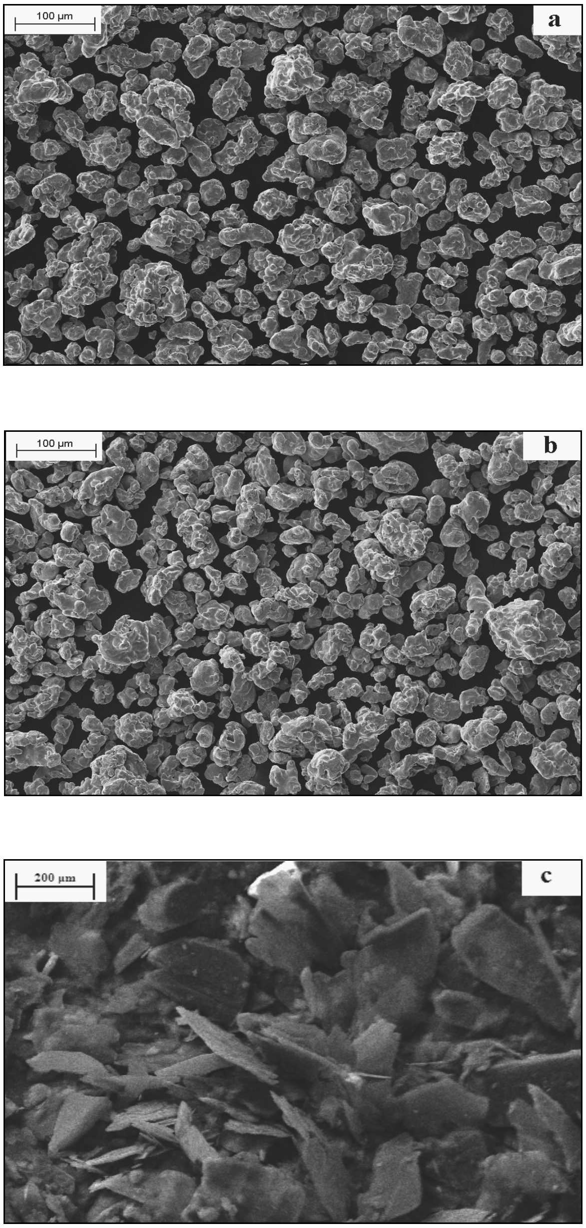


Fig. 3. Micrographs of base powders: a) Astaloy CrL pre-alloyed powder, b) Astaloy CrM pre-alloyed powder, c) GR12 graphite powder

Table 1.
Elements concentrations (wt.% and at.%) of chosen samples with using scanning electron microscopy (SEM/EDS)

Kind of powders	Sample symbol	Mo[%]		Cr[%]		Fe[%]	
		Wt.%	At.%	Wt.%	At.%	Wt.%	At.%
Astaloy CrL	*A	0.53	0.31	1.76	1.89	97.71	97.80
Astaloy CrM	**B	0.70	0.41	3.58	3.84	95.72	95.74

* A - steels compacted with 500MPa pressures, sintered at 1120ºC for 30 min in a vacuum, cooled in a nitrogen with rapid cooling
**B - steels compacted with 600 MPa pressures, sintered at 1120ºC for 30 min in a vacuum, cooled in a nitrogen with rapid cooling

Prepared green compacts were given in a process of sinter - hardening when keeping up the following parameters:

- debinding process was performed for 8 hours in fully nitrogen atmosphere in a separate plain furnace, before the sintering process. Green compacts were kept in the furnace of the 550ºC for one hour to remove the largest possible fraction of lubricant;
- green compacts were sintered at 1120ºC for 30 minutes in a vacuum furnace ($5.0 \cdot 10^{-1}$ mbar);
- sintered compacts were rapidly cooled nitrogen with two different rates: high cooling (with a rate 7ºC/s) and medium cooling (with a rate 1.6ºC/s) (Fig. 4);
- sintered compacts were tempered in a vacuum in the same furnace (at 200ºC for 60 minutes) and cooled in a nitrogen.

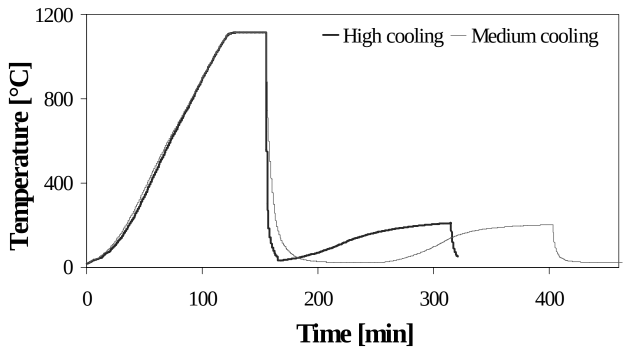


Fig. 4. Samples were sintered and cooled with two different rates and finally tempered

Density of sintered samples was measured on the basis of volume and mass of samples. Moreover, Archimedean (densimetric) method was used to evaluate the densities of sintered samples.

Microstructure sintered steels was investigated using light optical microscopy (LOM) and scanning electron microscopy (SEM), after polishing samples and metallographic etching with Nital 5%. Moreover, powders steels and graphite morphology was carried out by using SEM. Observation of investigated samples was carried out by using scanning electron microscopes ZEISS SUPRA 35 and OPTON DSM 940. To obtain the images the Secondary Electrons (SE) and Back Scattered Electrons (BSE) were used with the accelerating voltage 15-20 kV. To analysis of chemical composition was made with use of Energy Dispersive Spectrometry (EDS) method and with utilization of detector OXFORD.

Phase composition analyses of investigated samples were made on the PANalytical X'Pert PRO diffractometer, using the filtered X-ray Co Kα, step 0.05, time of counting 10 sec. at the voltage of 40 kV and tube current of 30 mA.

Micro hardness (HV0.1) test was done on each surface using Vickers hardness indenter. Research was carried out with load equal 100 g. Charpy test was performed on all samples at room temperature.

The investigation of wear resistance of tested materials was performed using disk-on-disk machine. During the test, the loss of mass of the samples was measured using laboratory balance. The measurements were done with 500 N load and 136 rpm speed, after 100 meters of total sliding distance.

3. Results and discussion

There have been prepared two different lots during sinter-hardening process. The green densities for the first lot with medium cooling were included in the range from 6.60 to 6.80 g/cm^3 (rectangular samples) and from 6.70 to 6.9 8 g/cm^3 (disk samples). The sintered densities were between 6.54 to 6.76 g/cm^3 (rectangular samples) and 6.69 to 6.97 g/cm^3 (disk samples). Sintered densities measured with Archimedes' principle (the measurement mass of a sintered material in air and water) were included in range from 6.71 to 6.89g/cm^3.

The green densities for the second lot with rapid cooling were included in the range from 6,54 to 6,82 g/cm^3 (rectangular samples) and from 6.71 to 7.0 g/cm^3 (disk samples). The sintered densities were between 6.51 to 6.78 g/cm^3 (rectangular samples) and 6.9 to 6.96 g/cm^3 (disk samples). Sintered densities measured with Archimedes' principle were included in range from 6.66 to 6.91 g/cm^3.

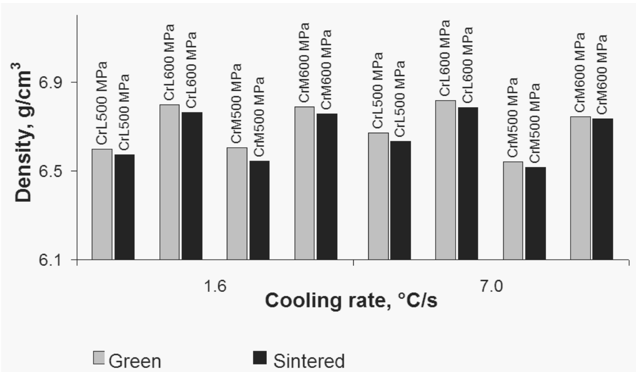


Fig. 5. Green and sintered density of studied compositions (rectangular samples); mean values

Among steels with different cooling rates the highest sintered densities equal 6.78 g/cm^3(for rectangular sample) and 7.0 g/cm^3(for disk sample) were achieved for steel CrL600MPa, cooled with rapid cooling. Figure 5 and 6 present sintered and green density of investigated powder mixtures. Densities obtained after sintering have characterized lower values what is consistent with specification has delivered from Höganäs company. Decreases sintered densities can be caused by applied sintering temperature, which has influence on porosity investigated steels. Figure 7 presents verified sintered densities with help of Archimedes' principle. It confirms that experiment was carried out correctly.

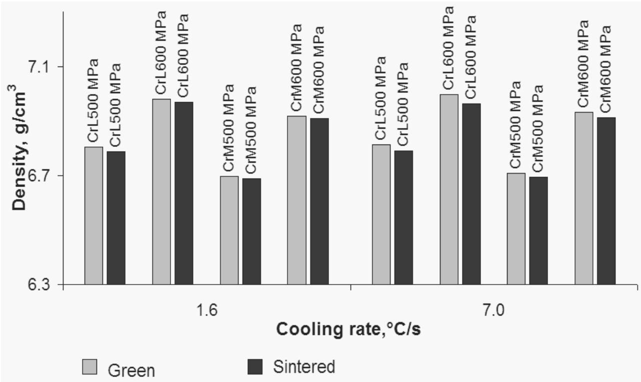


Fig. 6. Green and sintered density of studied compositions (disc samples); mean values

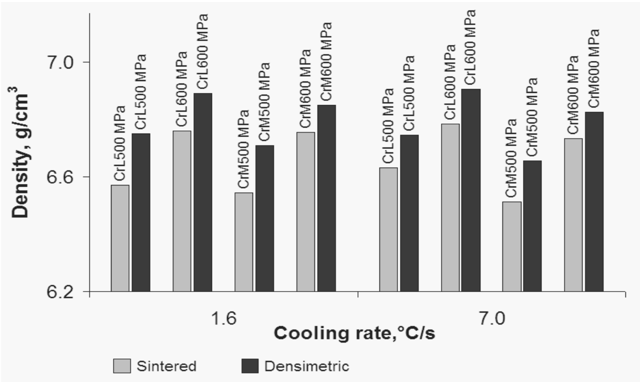
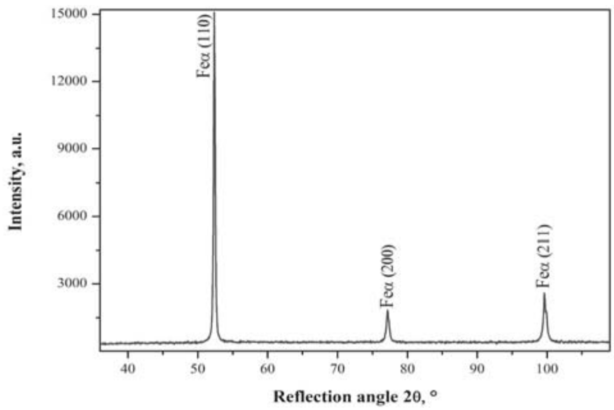


Fig. 7. Comparison between sintered density and density measured with Archimedes' principle of studied compositions (rectangular samples); mean values

Metallographic observation of steels was carried out after polishing and etching with Nital 5%. It could be noticed that all tested materials after the applied process of sinter-hardening proved to have different microstructures, depending on the cooling rate.

The sinter-hardening process of first lot of samples, cooled with medium cooling, determined the formation of mainly ferrite-perlite microstructures. Microstructures obtained for Astaloy CrL(0.2%Mo-1.5%Cr-0.6%C) steels with pressures of pressing 500MPa and 600MPa are presented in order a ferrite-perlite and ferrite-perlite with some tracks of bainite microstructures. Microstructures obtained for Astaloy CrM(0.5%Mo-3%Cr-0.6%C) steels with pressures of pressing 500MPa and 600 MPa are presented in both cases ferrite-perlite with some tracks of bainite microstructures (Figures 9 a, c). Figure 9 (b, d) present microstructures after SEM analysis. Figure 8a is presented XRD pattern of CrL 500 MPa, medium cooling, there were only found Feα peaks.



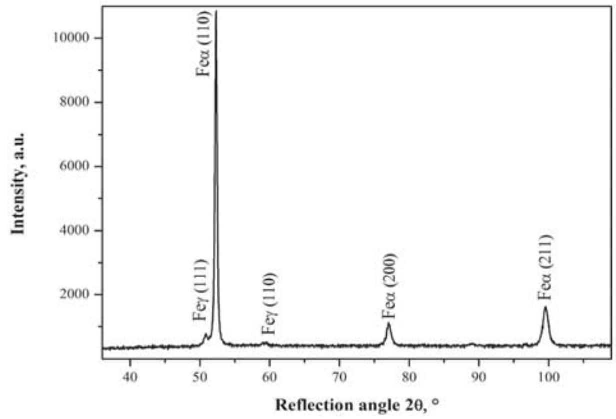


Fig. 8. X-ray diffraction pattern of: a) CrL 500 MPa, medium cooling; b) CrM 500 MPa, high cooling

The sinter-hardening process of the second lot of samples, cooled with rapid cooling, resembled probably the formation of ferrite-bainite-perlite microstructures. Microstructures obtained for Astaloy CrL(0.2%Mo-1.5%Cr-0.6%C) (Figures 9 e, g) steels compacted with pressures 500MPa and 600MPa are resembled in order ferrite-bainite-perlite and bainite-ferrite microstructures. Microstructures obtained for Astaloy CrM (0.5%Mo-3%Cr-0.6%C) steels compacted with pressures 500 MPa and 600 MPa are resembled in both cases ferrite-bainite microstructures. Figure 9 (f, h) present microstructures after SEM analysis. Figure 8b is presented XRD pattern of CrM 500 MPa, high cooling, there were found Feα and Feγ peaks.

The measurements of microhardness performed on studied materials were led on crosswise section on each surface, starting from 3 mm and continuing each 2 mm up to the centre. The highest value with loading 100g was achieved for Astaloy CrM (600 MPa) steel, cooled with rapid cooling. There are slight differences between results of measurement for steels cooled with two cooling rates. These differences could have come from porosity, which characterised these materials or on internal mixing these powders. Figure 10 presents microhardness of studied materials.

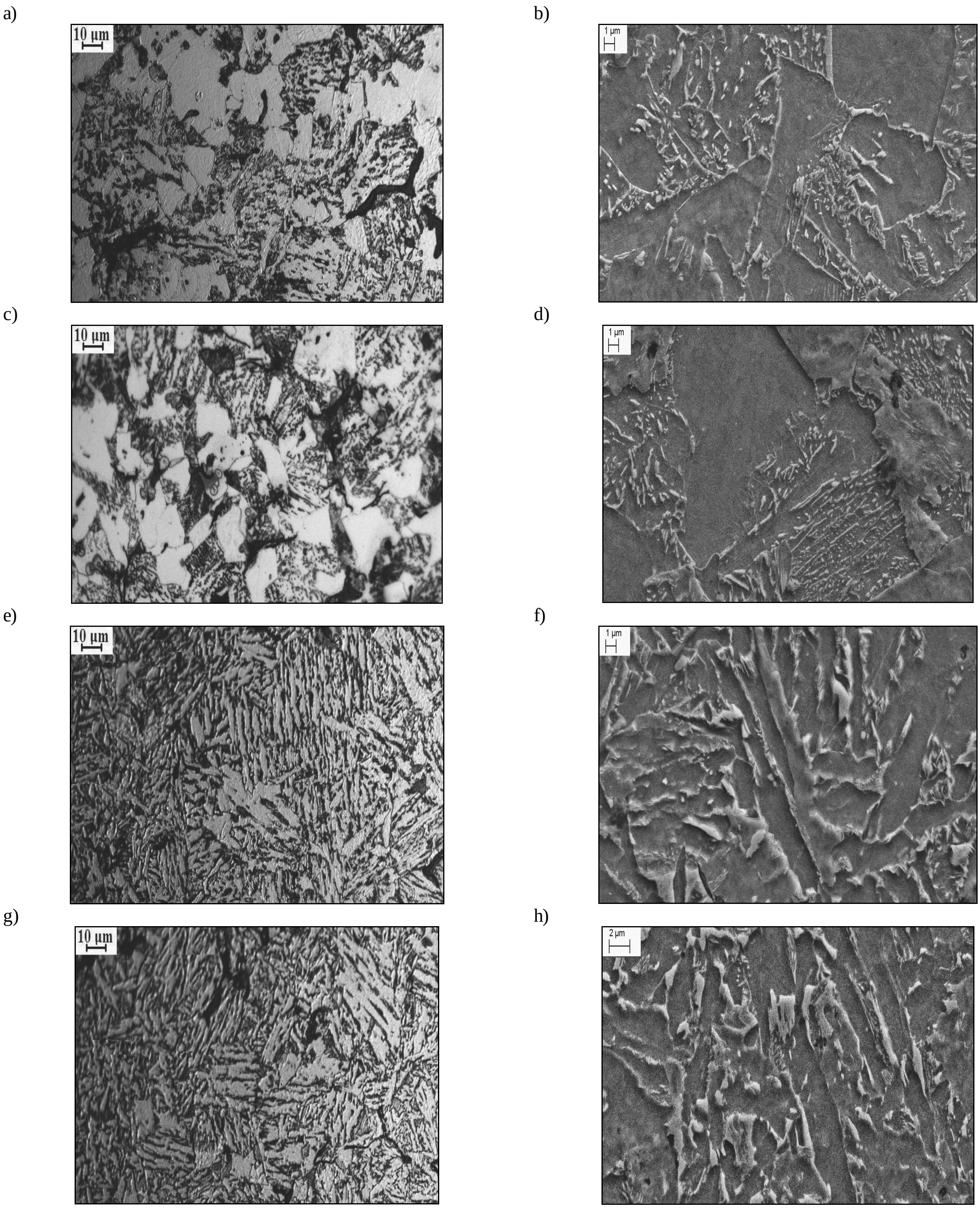


Fig. 9. Microstructure of sintered steels: a,b) Astaloy CrL 500MPa, medium cooling; c,d) Astaloy CrL 600MPa, medium cooling; e, f) Astaloy CrL 500MPa, high cooling; g,h) Astaloy CrL 600MPa, high cooling ; a, c, e, g) light optical microscopy (LOM); b, d, f, h) SEM

Higher values of impact energy were achieved for materials cooled with medium cooling, but there are slight differences between results of measurements for these two lots (Fig. 12). The highest values of impact energy were achieved for materials Astaloy CrM (600 MPa), where max. value is equal 12.46 J. The same values of impact energy were achieved for materials Astaloy CrM (500MPa) with rapid and medium cooling, where average value is equal 9.07 J.

The next step was to measure the wear resistance. In the first case (steel cooled with rapid cooling) disk on disk wear tests presents relative mass loss for a CrL 500 MPa steel (Fig.12). The most resistant to abrasion was composition for a CrM 500 MPa (medium cooling) steel where mass loss was only 0.20%. In other case (steel with medium cooling) disk on disk wear test shows relative mass loss for CrL 500 MPa steel (Fig.13). The most resistant to abrasion was composition for CrM 500 MPa (rapid cooling) where mass loss was only 0.022% .

The wear test shows, that a higher cooling rate provides insignificant harder materials (Fig. 10) rather than a lower cooling rate. Beside an abrasive disk, before and after wear tests in both lots of samples, confirmed also almost the same mass loss. The mass loss equal 0.001% was obtained with both: high and medium cooling rates. In picture 14 is present a chosen sample used in wear resistance test. Moreover, steels obtained from experimental mixtures, especially Ataloy CrM reveal better resistance to abrasion rather than Astaloy CrL in both cases of applied cooling rates. It is generally known that green samples pressing with higher pressure should reveal better mechanical properties, but Astaloy CrM 600MPa steels in comparison with lower pressure (500 MPa) cooled with two rates, show worse a resistance to abrasion (Figs. 12 and 13), what can be saddled with erroneous measurements.

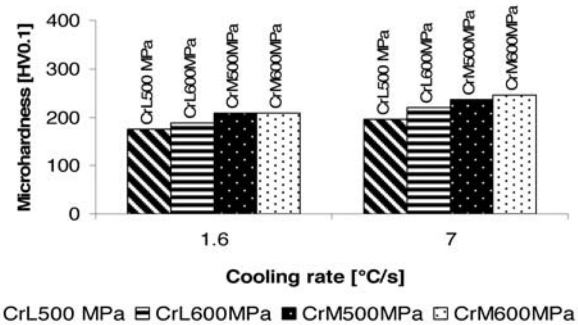


Fig. 10. Microhardness carried out on studied steels; mean values

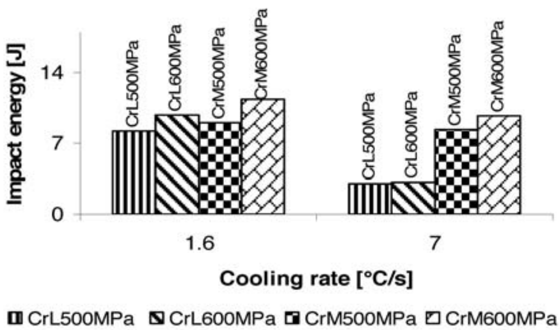


Fig. 11. Charpy impact test performed on materials with medium and rapid cooling

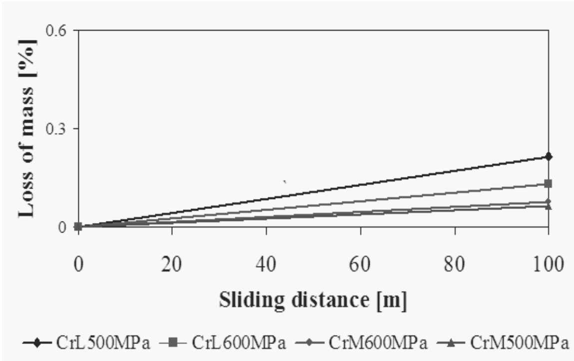


Fig. 12. Loss of mass in a function of sliding distance for the steel cooled with rapid cooling

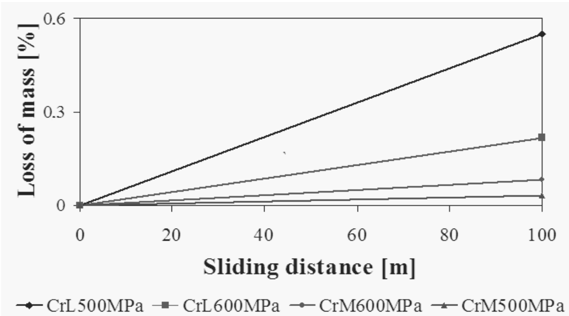


Fig. 13. Loss of mass in a function of sliding distance for the steel cooled with medium cooling

a) b)

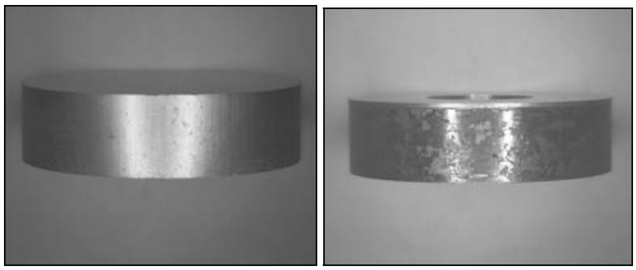


Fig. 14. Example of chosen sample (Astaloy CrL 500MPa, medium cooling) used in wear resistance test; a, b – sample before and after analysis

4. Summary

Investigations of CrL and CrM sintered steels alloys proved that: application of different cooling rates effecting the formation of different microstructures and because of this, also properties.

There was observed that a higher cooling rate provides insignificant higher materials wear resistance than a medium cooling rate. The highest value was obtained for a CrL 500 MPa sample (rapid cooling) for wear resistance test (using disk on disk test). Higher cooling rate directly influence on the structure of tested samples. Those which were cooled down with a higher cooling speed have resembled mainly ferrite-bainite-perlite structures and those with medium cooling rate have ferrite-perlite microstructures. There are slight differences between results of cross-section and surface measurements for materials cooled with two cooling rates.

Moreover, study of known materials (their chemical compositions) is faced with the needs to produce materials with improved strength, higher densities and higher surface hardness.

Acknowledgements

Investigation were partially realized within the framework on the Erasmus Programme, in Politecnico di Toriono, Campus Alessandria, Italy.

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