EFFECTS OF SUB- ZERO TREATMENT APPLIED TO SINTERED STEELS

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Treatments applied at low temperatures to the hardened steels are intended to increase their hardness, resistance to wear and dimensional stability due to a reduced amount of retained austenite and increase of the tetragonality of martensite. This paper presents the experimental results on the effect of applying a sub-zero treatment at 197K on sintered steels with various carbon content (0.54; 0.75 and 0.92% C) which have been previously given an oil-quenching heat treatment. A hardness increase by 8.56 up to 14.81 % as well as a decrease by 81% in the amount of retained austenite have been recorded when applying the sub-zero treatment.

Keywords: sub-zero treatment, powder metallurgy, sintered steel, retained austenite

1. Introduction

Sub-zero tempering represents a class of low-temperature heat treatment which is divided into two groups, namely: cold treatments applied at temperatures up to 153K (-120^{o}C) and cryogenic treatments applied at temperatures below 123K (-150^{o}C) [1, 2, 3].

These treatments are applied especially on quenched steels which have a high content of retained austenite (A_{ret}) in order to obtain partial or total transformation of it into martensite and also for increasing the martensite tetragonality. In this way it is expected to increase the hardness, the wear resistance and dimensional stability of steels [4, 5, 6, 7].

For powder metallurgy products the treatments at low temperature are less practiced. According to the data of the specialty literature, the cryogenic treatments are mainly applied to sintered carbide products type WC-Co (Widia

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tipes) [8-10] or to surface coatings consisting of TiC, TiCN, Al_2O_3 made by PVD or CVD [11, 12]. It was found that application of the cryogenic treatments to the Widia tips increases the amount of carbides as a result of precipitation of new phases such W_3Co_3C, η W_6Co_6C or η [13]. As a result the hardness and wear resistance of these products are increased and consequently their duration of operation is augmented by 9.58 to 21.8 % and the cutting speed raises up to 200 ÷ 350 m/min. [14, 15].

Concerning the application of sub-zero treatments to sintered steels it can bring specific benefits because the quenching of sintered steels has peculiarities different from the quenching of conventional steels. Thus cooling of the sintered steels from the austenitising temperature is usually practiced in oil unlike the one practiced for conventional steels for which the commonly used quenching medium is water or salt water. The reason for avoiding water or salt water when quenching sintered steels lies in the fact that such fluid liquids are easily absorbed into the pores and causes accelerated corrosion in a couple of hours [16, 17].

However oil quenching that is mandatory for sintered steels for the above mentioned reasons ensures a lower cooling speed, thus reducing the possibility of attaining the M_f point and therefore more retained austenite A_{ret} will be present along with martensite.

On the other hand in the last 10-15 years a new quenching procedure has been developed for sintered steels termed Sinter Hardening where cooling in view of quenching is achieved with a gas jet. In this instance an even larger amount of retained austenite is to be expected [18, 19].

For all these reasons the research in this paper was focused on the study of the effects of the sub-zero treatments intended to diminish the amount of retained austenite in some previously oil quenched sintered steels. More specifically investigations have been undertaken to elucidate the structural evolution as well as hardness and toughness changes of sintered steels with a carbon content in the range 0.54 up to 0.92% C. The samples were investigated in three treatment condition, namely: as sintered; sintered + oil-quenched ; sintered + oil-quenched + sub-zero treated at 197K (-76^{o}C).

2. Experimental

The sintered steels have been made by homogenizing a powder mixture consisting of iron powder type DWP 200, graphite and zinc stearate (denoted St-Zn in what follows, used as a binder and lubricant) in the following amounts:

Fe+0.6% *Gr*+2% *St Zn*
Fe+0.8% *Gr*+ 2% *St Zn*
Fe+1.0% *Gr*+2% *St Zn*

Homogeneous mixtures were compacted by pressing at 650 MPa in rectangular 10x10x55 mm sized molds.

The green compacts were sintered in the conditions specified in Table1. After sintering (denoted **S**) the sintered samples were oil-quenched (denoted **OQ**) according to the process parameters specified in Table 2 and finally subjected to the sub-zero treatment (denoted **Z**) in the conditions specified in Table 3.

Table 1

Applied Sintering Conditions

	Parameters	**Designation**
Sintering Temperature	1150^{o}C	
Time at Temperature	60 min	**S**
Atmosphere	Argon	
Cooling Rate	0.8^{o}C/min	

Table 2

Applied Quenching Parameters

	Parameters	**Designation**
Austeniting Temperature	860^{o}C	
Time at Austeniting Temperature	15 min	
Atmosphere	Argon	
Quenching	Oil	**OQ**

Table 3

Sub-zero Treatment Conditions

	Parameters	**Designation**
Sub-zero Temperature	197K	
Time at Temperature	60 min	**Z1**
	120 min	**Z2**
Cooling Rate	25^{o}C/min	

The procedure applied for the sub-zero treatment was as follows:

- oil quenched sintered steel samples were degreased by successive immersion in cold and hot benzene and then dried at 110^{o}C for the elimination of the infiltrated oil in pores during the oil-quenching operation ;

- sub-zero treatment was carried out in a mixture of dry ice (solidified CO_2) and technical alcohol;

- to maintain the proposed 173K temperature, dry ice was added during the long sub-zero treatment, namely 60 minutes and 120 minutes respectively;

- sub-zero treatment was carried out in a thermally insulated box.

3. Results and Discussion

As specified above, samples were obtained in three structural conditions as follows:

S- as sintered

S+OQ - sintered and oil quenched

S+OQ+Z1 -sintered, oil quenched and cooled in dry ice for 60 min

S+OQ+Z2 -sintered, oil quenched and cooled in dry ice for 120 min

For all samples the following characteristics have been determined:

- apparent density measured according to ISO 2738:1999
- porosity (by calculation)
- optical microscopically analysis according to ISO/TS 14321:1997
- amount of micro constituents (by means of quantitative image analysis)
- HV30 hardness measured according to ISO 4498:2010
- dynamic toughness (resilience) measured according to ISO 5754:1978
- structural carbon C_s in %, (calculated by means of quantitative image analysis)

Table 4 gives the values of the physic-chemical characteristics (apparent density and porosity) of the samples in the three structural conditions. Also indicated is the carbon content in % incorporated in the metallic structure of the sintered steels (denoted C_s) and the content of graphite in % which has not reacted with iron during the sintering process (denoted remaining graphite).

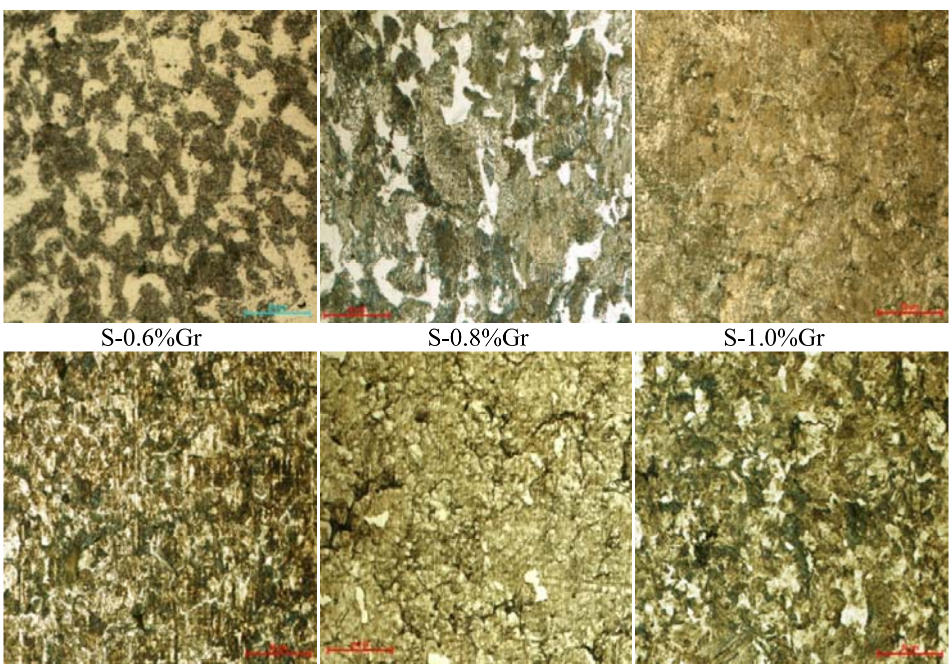
Table 4

Experimentally measured physico-chemical characteristics of the investigated samples

Sample	Apparent density [g/cm^3]	Porosity [%]	Structural carbon C_s[%]	Remaining Graphite Gr [%]
S - 0.6% Gr	6.79	12.97	0.54	0.03
S - 0.8% Gr	6.80	12,88	0.75	0.04
S - 1% Gr	6.78	13.11	0.92	0.02

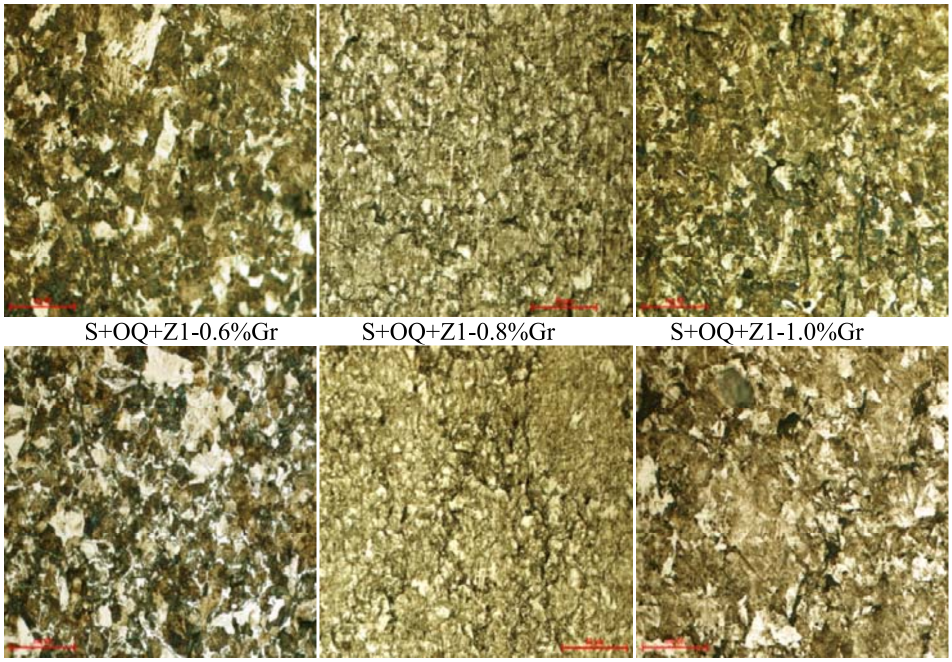
S +OQ - 0.6% Gr	6.82	12.56	0.54	0.03
S +OQ - 0.8% Gr	6.79	11.53	0.75	0.04
S +OQ - 1% Gr	7.11	8.85	0.92	0.02
S +OQ+Z1-0.6% Gr	6.83	12.43	0.54	0.03
S +OQ+Z2-0.6% Gr	7.13	8.59	0.54	0.03
S +OQ+Z1-0.8% Gr	6.83	12.43	0.75	0.04
S +OQ+Z2-0.8% Gr	6.85	12.17	0.75	0.04
S +OQ+Z1-1% Gr	7.08	9.23	0.92	0.02
S +OQ+Z2-1% Gr	7.11	8.85	0.92	0.02

The series of micrographs in Fig.1 depict the microscopic structure for the sintered samples with various carbon content and treated in the three above mentioned structural conditions (S-as sintered; S+OQ- sintered and oil quenched; S+OQ+Z1-sintered, oil quenched and cooled in dry ice for 60 min; S+OQ+Z2 - sintered, oil quenched and cooled in dry ice for 120 min).



S-0.6%Gr S-0.8%Gr S-1.0%Gr

S+OQ-0.6%Gr S+OQ-0.8%Gr S+OQ-1.0%Gr



S+OQ+Z1-0.6%Gr S+OQ+Z1-0.8%Gr S+OQ+Z1-1.0%Gr

S+OQ+Z2-0.6%Gr S+OQ+Z2-0.8%Gr S+OQ+Z2-1.0%Gr

Fig.1 Microstructures of sintered steels samples etched with NITAL 2% and PICRAL 2%

Table 5 gives the results of the quantitative image analysis applied in order to determine the amount of the various structural micro constituents identified in Fig. 1 in the sintered steels in various structural conditions (F=ferrite, P=perlite, Cem=cementite, B=bainite, M=martensite, A_{ret}=retained austenite). Error determination is ~ 3%.

Table 5

Results of the quantitative image analysis in the investigated sintered steels

In-going graphite [%]	Cs [%]	Structural condition	F [%]	P [%]	Cem [%]	B [%]	Martensite		Retained austenite	
							M [%]	(+)ΔM [%]	A_{ret} [%]	(-)ΔA_{ret} [%]
0.6	0.54	S	25.21	73.12	-	-	-	-	-	-
		S+OQ	21.65	8.91	-	14.34	43.62	-	9.64	-
		S+OQ+Z1	20,52	8.74	-	14.08	48.76	10.54	5.93	38.49
		S+OQ+Z2	20.67	3.91	-	15.21	56.38	13.52	2.78	53.12

0.8	0.75	S	2.24	97.48	-	-	-	-	-	-
		S+OQ	2.08	11.16	-	18.19	55.31	-	11.54	-
		S+OQ+Z1	2.13	4.48	-	17.25	67.16	17.64	8.81	29.12
		S+OQ+Z2	2.12	1.74	-	17.12	75.51	11.06	2.41	70.54
1	0.92	S	-	96.12	3.74	-	-	-	-	-
		S+OQ	-	4.58	3.92	8.15	65.88	-	16.38	-
		S+OQ+Z1	-	4.12	3.87	8.41	74.14	11.14	7.92	51.64
		S+OQ+Z2	-	4.15	3.65	9.12	79.57	6.82	1.51	80.93

The results on the mechanical properties obtained in various structural conditions for samples with different carbon content are presented in the series of figures 2-5.

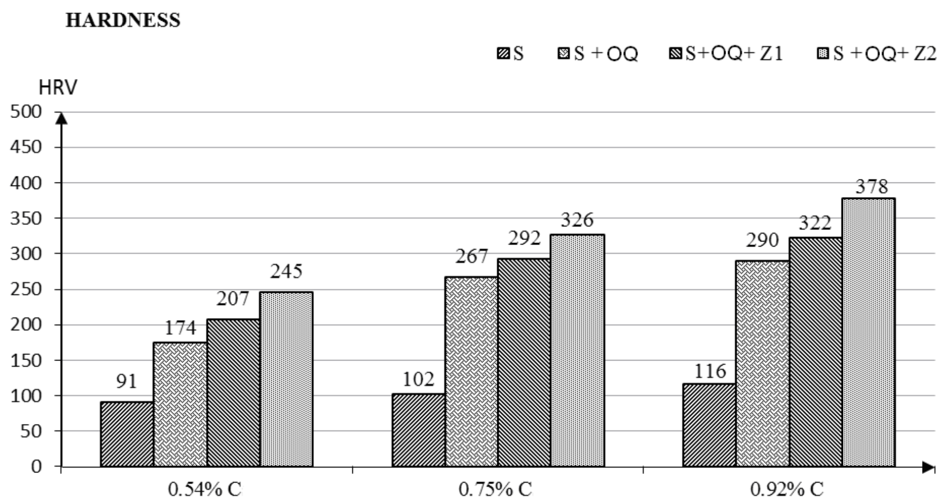


Fig.2. Vickers hardness results (expressed in daN/mm^2) for the investigated steel samples with different carbon content and various structural condition

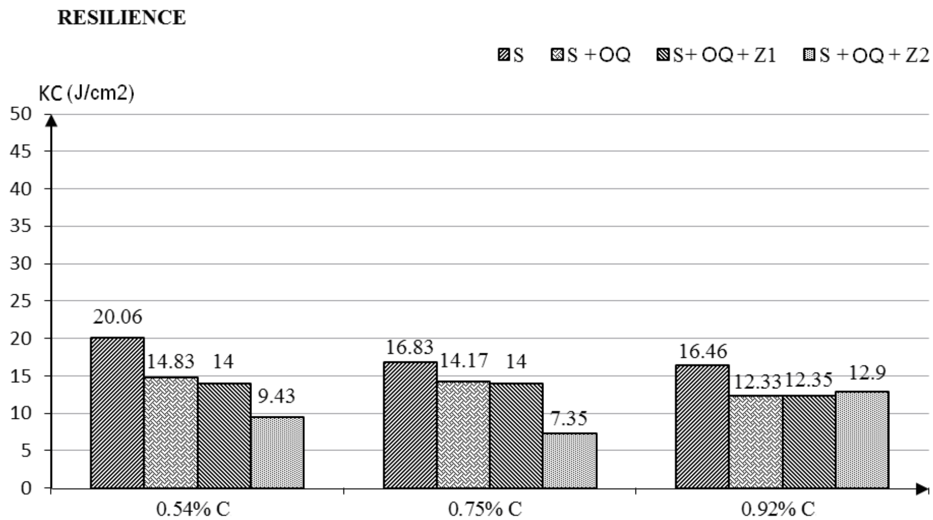


Fig.3. Dynamic toughness results (expressed in J/mm^2) for the investigated steel samples with different carbon content and various structural condition

In the Fig.4 is presented the evolution of samples hardness and in Fig.5 the evolution of the retained austenite for various heat treatments and dependent on the carbon content.

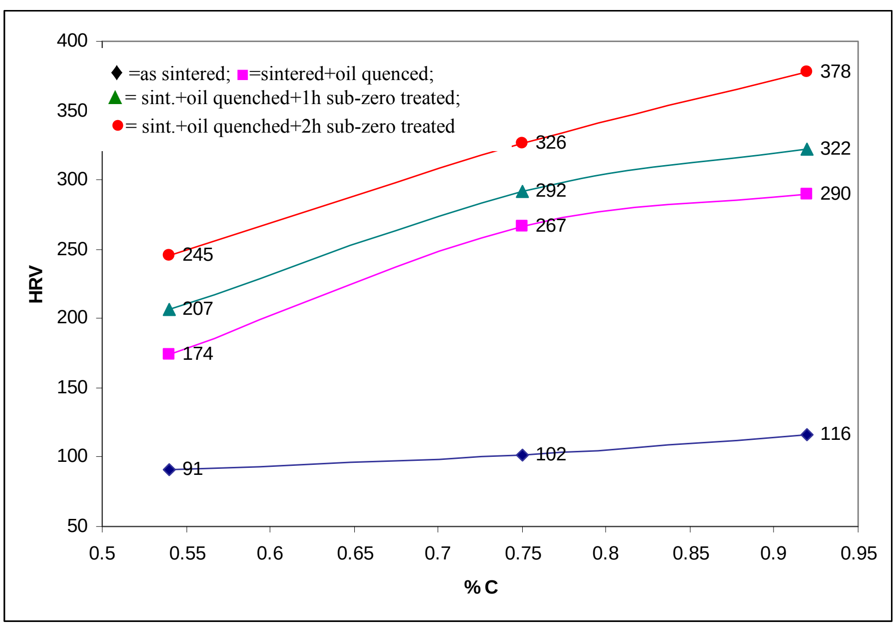


Fig.4.Hardness dependence on carbon content for the sintered steels in various treated conditions

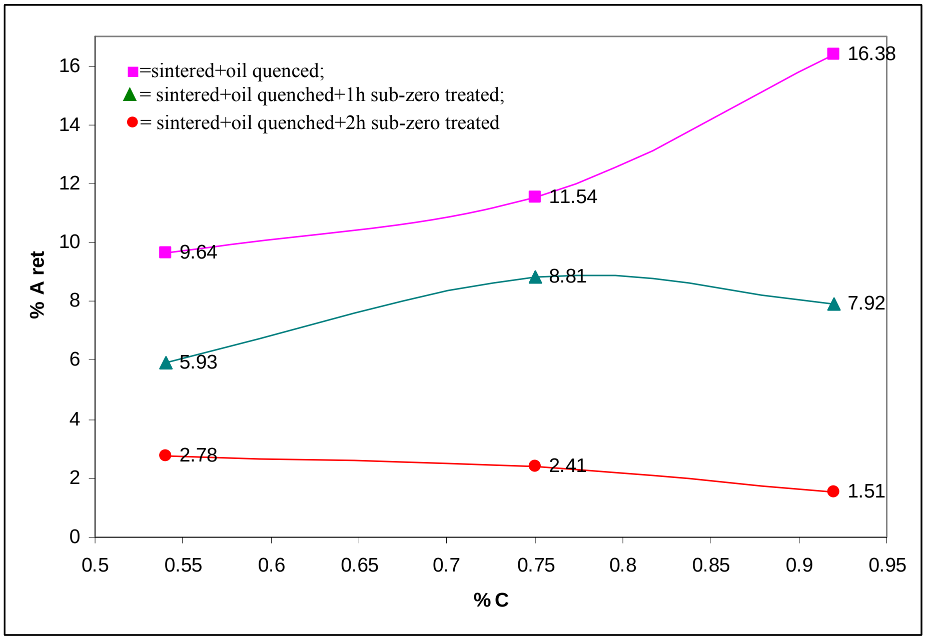


Fig.5. Amount of retained austenite versus carbon content of the sintered steels in various treated conditions

The different curves in Fig.4 clearly show that the hardness of the sintered steel samples is influenced in a far higher degree by the heat treatment (including the sub-zero treatments) in comparison with the influence exerted by the carbon content in the sintered steel.

Indeed according to the data in Table 5 the impressive hardness increase brought about by oil quenching applied to the sintered steels (pink curve in Fig.4) is to be expected because of the transformation of pearlite into the hard bainite and martensite. But what's really remarkable in Fig.4 is the noticeable difference in hardness between the pink curve and the red curve brought about by the increase of the duration of the sub-zero heat treatment from 1 hour to 2 hours.

A close examination of the experimental data in Table 5 gives the explanation for this increase in hardness induced by the sub-zero treatment. This hardness increase is to be ascribed to the impressive decrease in the amount of soft retained austenite. Actually the upper three curves in Fig.4 compare well with the curves in Fig.5 (amount of retained austenite in various treatment conditions). Taking into consideration the values in Fig.4 and 5 one may appreciate that a maximum hardness increase of 88 Vickers units is brought about by a decrease of 16% in the amount of retained austenite (from 16.38 to 1.51%) as indicated for the sintered steel containing 0.92%C.

Some special considerations have to be taken into account when appreciating the effect of heat treatments as well as sub-zero treatments in sintered steels. Steels made by powder metallurgy have a more complex structure after quenching in comparison with conventional steels. Indeed the presence of intercommunicating pores in the sintered structure may establish a microscopic non-uniformity in the cooling rate throughout the sintered product. Indeed absorption of the liquid coolant into the intercommunicating pores makes the cooling rate higher at the pores surface than in deeper regions. As a consequence martensite and retained austenite are preferentially formed around these internal interfaces while in deeper areas bainite and even unchanged perlite are expected to be found.

Another peculiarity of sintered steels obtained by chemical reaction between iron and graphite as the ones investigated in this research consists in the presence of carbon gradients induced by the presence of internal interfaces between the original reactants. This chemical micro-inhomogeneity may induce additional differences in the response to heat treatments and subzero treatments for sintered steels in comparison with conventional steels.

4. Conclusions

1. Sintered steel samples have been made by compaction and chemical reaction during sintering between chemically pure components (iron and graphite). A high degree of reaction has been obtained as indicated by the high values of the structural carbon content Cs which were very close to the amount of graphite in the original powder mixture.

2. Oil quenching followed by sub-zero treatments at 197K has been applied in sequence to sintered samples with different structural carbon content (0.54; 0.75 and 0.92%C).

3. Optical microscopically observation coupled to quantitative image analysis has indicated complex microstructures in all as quenched samples (pearlite, bainite, martensite, retained austenite, accompanied either by free ferrite or by free cementite, depending on the carbon content).

4. Sub-zero treatments at 197K have pointed to an increased efficiency in transforming the soft retained austenite into hard martensite when the duration of the treatment was augmented from 1 hour to 2 hours. The 1 hour sub-zero treatment has succeeded to diminish the amount of retained austenite to 2/3, 3/4 or even to 1/2 of its initial content in the oil quenched samples, depending on the carbon content. The additional duration in the 2 hours sub-zero treatment was even more efficient as it induced even higher decrements in the retained austenite content especially for the eutectoid sintered steel. The highest effect of the 2 hours sub-zero treatment in reducing the amount of retained austenite was manifest for

the hypereutectoid 0.92%C sintered steel (from 16.38% to 1.51% retained austenite).

5. Vickers hardness values measured in sub-zero treated sintered steels were in good correlation with the amount of retained austenite. The hardness increments induced by the 1 hour treatment were roughly half the ones produced by the 2 hours treatment. Again the highest effect of the 2 hours sub-zero treatment in increasing the hardness was manifest for the hypereutectoid 0.92%C sintered steel (a 88 Vickers units increase in comparison with the oil-quenched condition).

R E F E R E N C E S

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