Proposed heat treatment conditions to improve toughness of steel grinding balls

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Following standard heat treatment, steel grinding balls possess hardness values greater than 60 Rockwell C in the case of 3 inch diameter balls. The internal zone is also hard and therefore has low toughness, reducing the working life of the ball. The objective of the present study was to improve the quality of 3 inch diameter grinding balls by producing higher surface hardness and a central zone with adequate toughness.
To achieve this, time-temperature-transformation diagrams were produced, and finite difference and finite element modelling of the temperature distribution within the balls during quenching and equalisation treatment were experimentally validated. From these, new heat treatment conditions were established to produce lower central hardness values, (53-55 HRC), while maintaining the surface values.
This resulted in 60% fewer in Drop Ball Test than balls processed by standard heat treatment.

KEYWORDS: STEEL GRINDING BALLS - HARDNESS - TOUGHNESS - QUENCHING TIME - IMPROVED WORKING LIFE

INTRODUCTION

Steel grinding balls of 3 and 5 inch diameter are the most commonly used sizes in the milling of copper ores. They are fabricated from steel rods austenised at 800° C followed either by roll-forming (3 inch balls) or by forging (5 inch balls). In both cases, the balls are then quenched in water at an initial temperature of 50° C and then equalised, (i.e. natural cooled in open air), to a uniform temperature. For the 3 inch diameter balls, the time for each of these treatments is 80s and 40s, respectively. The structure of the balls after final cooling is martensite with some retained austenite [1].. Since grinding balls are subjected to wear, abrasion and impact, the desirable goal of heat treatment should be to ensure that they have properties appropriate to the operational conditions under which they are to be used: lower residual stress; a high degree of hardness and wear resistance in their surface zone; and an adequate toughness in their central zone to enable them to absorb some impact energy without cracking.

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For typical 1% carbon steel containing alloy components such as Mn, Cr and V, 3 inch balls would be expected to have a surface hardness in the order of 65 RC, associated mainly with a martensitic microstructure; however, manufacturers' quality standards only specify 65 RC as the maximum hardness available, together with an acceptable minimum value of 60 RC [2]. In addition, both the producers and users of grinding balls normally claim that the volumetric hardness of the balls should have a standard quality similar to the surface hardness, as can be seen in Table 1[2]. This implies that not only the surface zones but also the central zones of the balls must be of high hardness. As a consequence, high tensile strength and low toughness is achieved, whereas in fact it is preferable to have a moderate hardness in the central zone to improve the impact resistance of the grinding balls. In addition, as the martensitic structure in the central zone of the balls forms only during the equalisation step of the manufacturing process, high residual stresses are generated when the volumetric dilatation associated with the austenite- to- martensite phase transformation during equalization is constrained by the martensitic external zone induced during quenching [3-8].
The residual stress during heat treatment of steel grinding balls has previously been modelled and analytically solved and validated. The final equations obtained were (more details can be found in references [1,3-8]):

$$u(r) = \frac{(1+\nu)\int r^2 F(r)dr}{r^2(1-\nu)} + C_1\frac{r}{3} + \frac{C_2}{r^2} \qquad (1)$$

$$\sigma_{rr} = \frac{E}{(1+\nu)(1-\nu)}\left((1-\nu)\frac{\partial u}{\partial r} + 2\nu\frac{u}{r} - (1+\nu)F(r)\right) \qquad (2)$$

where u is the radial displacement at position r; ν is the Poisson's modulus; F(r) is a thermo- mechanical function that involves linear contraction during cooling and expansion due to austenite-martensite phase transformation; σ_{rr} is the radial stress; E is the elastic modulus of the austenite-martensite mix, determined experimentally from tensile tests at temperatures between 50° C and the martensitic start temperature, Ms; C_1 and C_2 are constants which are determined from the following border conditions:

- At surface of the balls, $\sigma_{rr} = 0$.
- If the centre of the ball has a temperature ≤ Ms, then at this position $\partial\sigma_{rr}/\partial r = 0$.
- If the temperature of the ball at a radius r ≥ Ms, then σ_{rr} (r ≤ r*) = 0, where r* is the radius for which T(r = r*) = Ms.

In addition, if for some radius r** the effective or equivalent stress σ_{ef}, (defined in this case as $\sigma_{ef} = |\sigma_{rr} - \sigma_{\theta\theta}|$, where $\sigma_{\theta\theta}$ is the circumferential stress), is equal to or greater than the yield stress of the steel σ_0, then $\sigma_{ef(r=r^{**})} = \sigma_0$, if $\sigma_{ef} < \sigma_R$ (rupture stress), or $\sigma_{ef(r=r^{**})} = 0$ if $\sigma_{ef} \geq \sigma_R$. Due to its low ductility, the rupture stress of the steel in the balls, is approximately equal to its tensile strength.
The radial distribution of circumferential stress is obtained from equation (2) and the force equilibrium from equation (3).

$$\frac{\partial\sigma_{rr}}{\partial r} + 2\frac{(\sigma_{rr} - \sigma_{\theta\theta})}{r} = 0 \qquad (3)$$

The hard, low-toughness central zone and the high residual stresses induced during heat treatment result in the balls having a shorter working life than is potentially possible.
The present study aimed at simulate the heat treatment of the 3 and 5 inch diameter balls and, in particular, improving the working life of 3 inch diameter steel grinding balls by producing it with a central zone of moderate hardness and adequate toughness, thereby reducing the need for ball replacement and so lowering mineral processing costs. While obtaining these requirements may seem simple, in fact it is far from it; for instance, if the cooling rate of the centre of the balls is much greater than the critical velocity of quenching, the whole ball would consist of martensite and retained austenite. However, it was reasoned that there may be an optimal heat treatment in which the central zone of the balls is quenched up to a temperature that would allow, during the equalisation, some proportion of the phase transformation of the austenite to occur above Ms. This would produce a structure with lower hardness and higher toughness, without affecting the surface hardness.

Table 1 - Standard hardness and chemical composition of 3 inch diameter grinding balls.

Hardness (RC)			Chemical Composition (wt..%)						
Surface min.	Surface max.	Vol. min.	C	Mn	$P_{max.}$	S_{max}	Si	Cr	Mo max
60	65	60	0.95–1.05	0.85–1.05	0.035	0.04	0.20–0.60	0.50–0.75	0.03

To accomplish this, 50 heat-treated 3 and 5 inch diameter balls were obtained from a company in Chile. The chemical compositions of two of these balls were determined by optical emission spectrometry (OES), and their surface and radial hardness were measured and the volumetric hardness calculated. As discussed below, the quenching rate at the centre of the 3 inch ball was low (6.6 °C/s on average). Consequently the continuous cooling transformation (CCT) curves of their steel approximated to the temperature- time- transformation (TTT) diagrams, determined theoretically in this work using the JMAT Pro software [9] and experimentally by differential scanning calorimetric (DSC) and metallographic analysis. Two mathematical models, explicit finite difference method (FDM) and finite element method (FEM), were then used to simulate the temperature distribution in a typical steel ball during quenching and equalisation. The modelled results were compared with experimental data. From this information, new heat treatment temperatures (or times) for the heat treatment of the 3 inch diameter balls were analysed with the aim of producing central zones with martensite–bainite structure and some retained austenite, and therefore with greater toughness. Drop Ball testing involving up to 4000 impacts was performed to two groups of 20 balls 3 inch diameter balls: one standard treatment group and one proposed treatment group. Finally, the distribution of the residual circumferential stresses following equalisation of both groups of balls was calculated from eqs. (1) to (3).

METHODOLOGY

To determine the chemical composition of the selected balls, two half-discs were cut from each ball while refrigerated. The chemical composition was determined by OES at three radial positions: periphery, semi-radius and centre. Their Rockwell hardness was measured at the surface and at points 3 mm apart along a radius, using a LECO hardness tester.
To obtain the TTT curves by a metallographic method, steel samples measuring 10x10x5 mm were taken from each ball and austenised at 800°C for 30 min in a vertical furnace with gas protection. Samples were then tempered at 300°,400°, 500°and 600°C in a stainless steel crucible containing a salt bath of 1.5 kg 15% NaCl for 600° and 500°C, and of 50% KNO_3 at 300° and 400°C. Samples were maintained at the above temperatures for different times, then immediately water-quenched. They were then polished, etched and observed metallographically; the images were analysed using Image J (64-bit) software to

determine the proportions of martensite and the remaining phase corresponding to the austenite transformation at each temperature.

DSC analysis using Netzsch equipment was conducted on 100 mg steel samples austenised at 800°C for 20 min, then cooled at 50°C/min to 700 or 600°C and maintained at those temperatures.

To model the temperature T of the balls, the following assumptions were made [1,3-8]:

- The balls were spherical and homogeneous, and only radial temperature gradients occur.
- The thermal conductivity K and the specific heat Cp of the steel depends on its temperature.
- The density ρ of martensite and austenite (or bainite) was assumed to be 7.75 g/cm^3 and 8.03 g/cm^3, respectively [7].
- The heat losses from the quenching water to the ambient air are negligible.

The heat equation for the temperature of the balls is then

$$K\left(\frac{\partial^2 T}{\partial r^2}\right)+\frac{2}{r}\frac{\partial T}{\partial R}=\rho\frac{\partial}{\partial t}\left(TC_p\right) \quad (4)$$

with the boundary conditions

$$\frac{\partial T}{\partial r}(0,t)=0$$

$$-K\frac{\partial T}{\partial r}(R,t)=h(T_s-T_{am})$$

where R is the ball radius, and h is the coefficient of heat transfer between the ball surface at a temperature Ts to ambient temperature, T_{am}. To solve equation (4) by explicit FDM, radial increments of R/20 and time increments of 0.02s for quenching and 0.05s for equalisation were adopted. The heating of the quenching water initially at 50° C was considered as was the heating of the balls during phase transformation from austenite to martensite.

During quenching, the coefficient of convective heat transfer **h** between the balls and the water varies with the temperature of the balls. In this case, cooling occurs in three steps: i) until the surface temperature of the balls is around 220ºC, radiation and convection heat transfer mechanisms across the vapour layer surrounding the balls is considered; ii) until a surface temperature of the balls is 105ºC, the cooling of the balls is produced by vapour transport from its surface; and step iii) begins when the surface temperature of the ball reaches the boiling point of the water, and the heat transfer mechanism becomes convection only[3-8, 10-11]. Typical **h** values during quenching vary between 10.000 W/m^{2}ºC (at lower and higher ball surface temperatures) and 60.000 W/m^{2}ºC, at a surface temperature of 300ºC [12]. During equalisation, the heat transfer mechanism from the surface of the balls to the air is natural convection, where **h** also depends on surface temperature, with an average value of 25 W/m^{2}ºC [13]..

The FEM modelling of the temperature changes, given by equation (4), was carried out using DEFORM-HT commercial software [14]. The model was constructed taking advantage of the spherical geometry. The heat transfer conditions were coupled with phase transformation using the properties and characteristics of the material predicted by the JMatPro simulation package. Also, in this case the coefficient of convective heat transfer between the ball and the water varied depending on the temperature of the ball. The temperature distribution during quenching and equalization was tested by inserting thermocouples at three different positions in the balls: centre, R/2, and near the surface, R-7mm. The temperature of the quenching water was continuously monitored during the process for comparison with simulated results. From the TTT diagrams and the temperature model during thermal treatment of the balls, four new thermal treatment temperatures (or times) were analysed for quenching and equalisation steps. The objective, as discussed, was to achieve not only martensite and retained austenite in the centre of the finished balls, which will result in a structure of lower hardness and greater toughness. To experimentally test the proposed temperatures, two 3 inch diameter balls for each of the four proposed conditions were coated with carbon to prevent decarburisation and austenised at 800°C for 3 h in a muffle furnace, then quenched and equalised at the current conditions of entry temperature and water flow and air temperature, but for the newly proposed temperature treatment. When this process was complete for each ball, half-discs were cut from them and their surface, volumetric and central hardness's were determined. Once the surface and central hardness's of the balls were measured satisfactorily, 20 balls were austenised and thermally treated under the new conditions. These 20 balls and a group of 20 standard balls were weighted and then successively subjected to up to 4000 cycles of a Drop Ball Tests from a drop of 5 meters. The weight loss and the fractured or cracked balls in each group were then noted.

RESULTS

In general, no significant differences in chemical composition were observed, either between the balls themselves or between locations within the balls. Table 2 shows the composition of the surface of the 3 inch diameter balls, which was consistent with those listed in Table 1.

Rockwell C hardness values of 62.5, 61.8 and 61.2RC were obtained for the surface, volumetric and central positions, respectively. The high central hardness value implies low steel toughness in that zone.

Tab. 2 - Measured chemical composition of 3 inch diameter ball.

Element	C	Mn	$P_{max.}$	S_{max}	Si	Cr	V	Cu	Ti
Composition (wt.%)	0.982	0.972	0.020	0.011	0.259	0.646	0.256	0.027	0.021

Figure 1 shows the experimental TTT diagrams for the 3 inch diameter balls, obtained from the DSC results and from micrographs as previously described. Ms temperature was 215°C.

Figure 2 shows the FDM simulated temperature distribution during quenching at the three radial locations, together with the observed thermocouple temperature values. The close agreement between the simulated and observed values is particularly notable at the centre (R=0mm) and at the intermediate position (R=19mm); however the observed near surface temperatures were affected by water entering the hole drilling to place the thermocouple and were therefore lower than predicted.

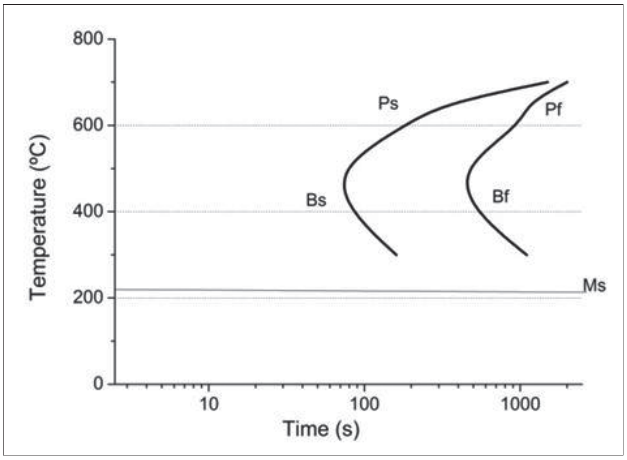

Fig. 1 - Experimental TTT diagram for the steel in the 3 inch diameter balls.(P= perlite; B=bainite; s=start; f=finish)

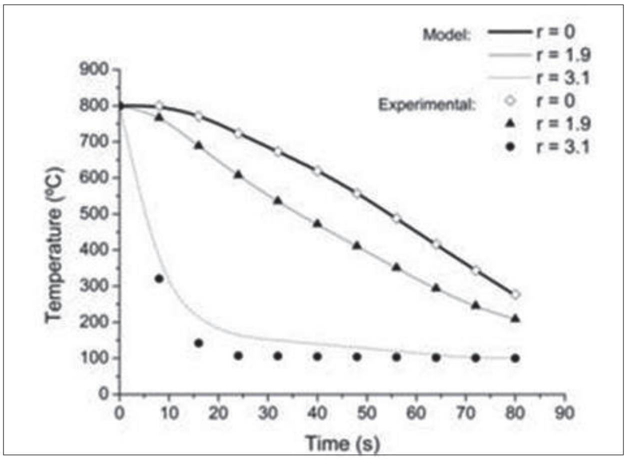

Fig. 2 - Temperature distribution simulated by FDM during quenching of 3 inch diameter balls.

The increment in temperature of the quenching water as a result of immersion of the balls of 3 inch diameter is shown in Figure 3.

Note the close agreement between theoretical and experimental values, being the theoretical temperature of the water lower than the measured, since the heat loss from the water to ambient air was not considered in the model.

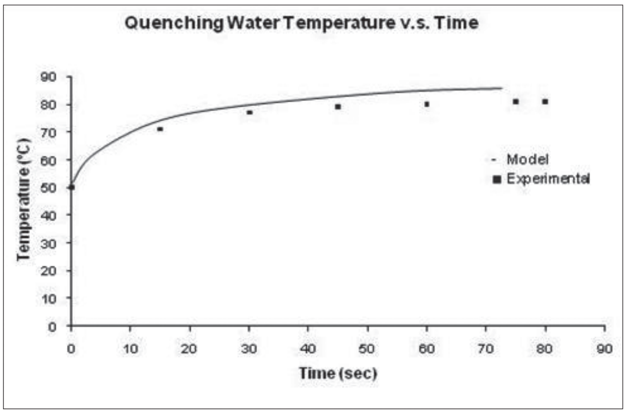

Fig. 3 - Increase in temperature of water during quenching of 3 inch diameter balls

Figure 4 shows the FEM simulated temperature distribution during quenching and equalisation at three radial locations for the: A) 3 inch and B) 5 inch diameter balls, superposed on observed values.

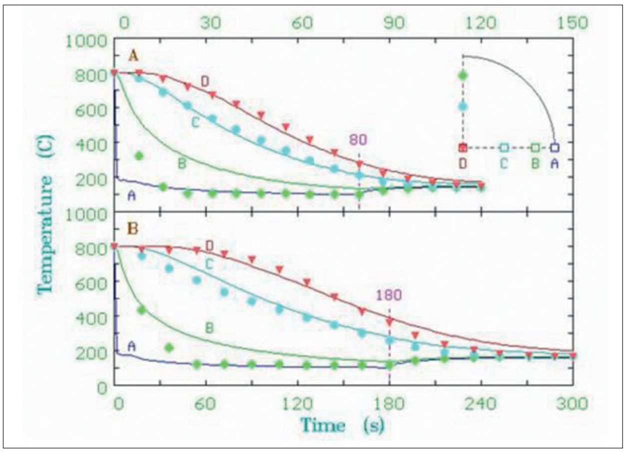

Fig. 4 - Temperature distribution simulated by FEM during quenching and equalisation of A: 3 inch and B: 5 inch diameter balls.

In figure 5 the comparisons between temperatures predicted by FEM and measured by thermocouples are plotted for 3 and 5 inch diameter balls. Almost all the data agrees within ±10%, as indicated by the dotted lines on the graph, with the exception of the values recorded by the thermocouple located close to the surface, affected by contact with the quenching water.

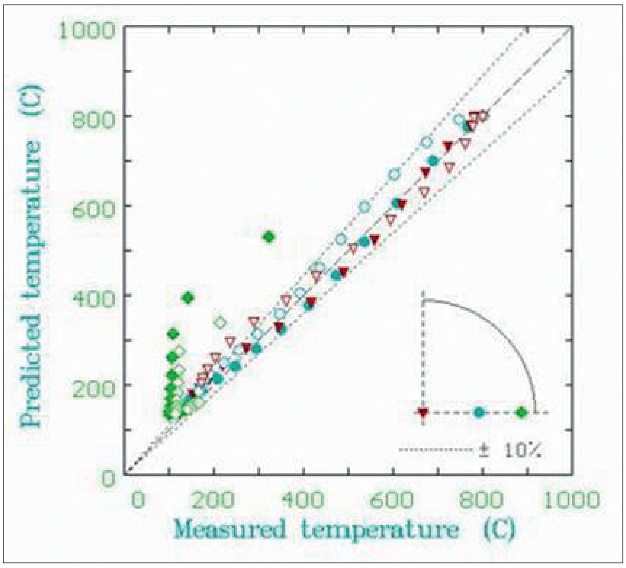

Fig. 5 - Comparison between temperatures predicted by FEM and measured by thermocouples in 3inch (filled symbols) and 5 inch diameter balls (open symbols).

Figure 6A and B shows the CCT curves predicted by JMatPro software based on the chemical composition of the steel of the 3 (Table 2) and 5 inch diameter balls assuming an austenite grain size of 50 μm and the cooling curves predicted by FEM. Note the acceptable agreement between the experimental TTT diagram, figure 1, and the theoretical CCT curves, figure 6 A, for the steel in the 3 inch diameter balls.

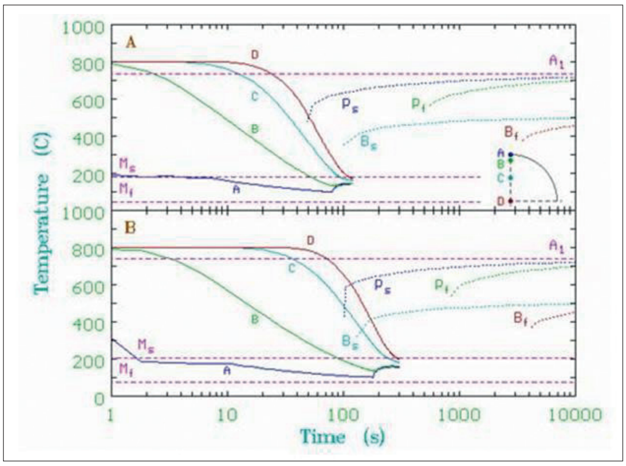

Fig. 6 - Theoretical CCT and cooling curves for balls: A, 3 inch diameter and B, 5 inch diameter.

The volume fraction of the various micro structural components in the 3 inch diameter balls are shown in Figure 7 as a function of the radial position and time, predicted by JMat Pro software. The distributions during quenching are shown in the upper plots (a is for 40s and b is for 80 s). The lower plots c and d show the fraction during equalisation, 20 s and 40 s after quenching.

Figure 8 shows the fraction transformed to martensite in 3 and 5 inch diameter balls as a function of distance from the surface and for different treatment times. Note that the times shown in this figure are measured from the start of the heat treatment, for example for ball A (3 inch diameter) 80s represents the end of quenching and thus 100s corresponds to 20s of equalisation.

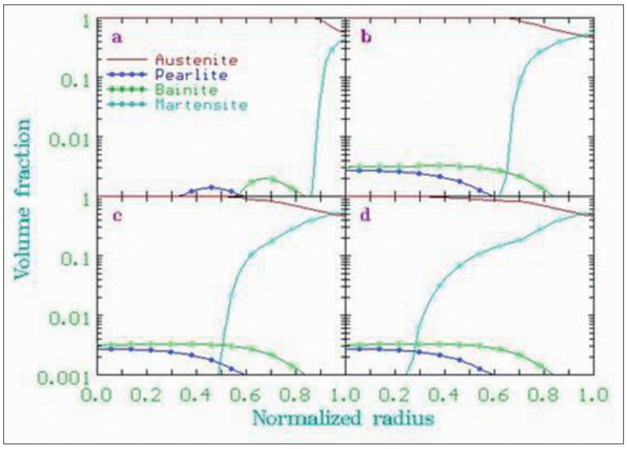

Fig. 7 - Volume fraction of the microstructural constituents as a function of radial position in ball A during quenching after (a) 40s and (b) 80s of this treatment; and equalisation after (c) 20 s and (d) 40 s.

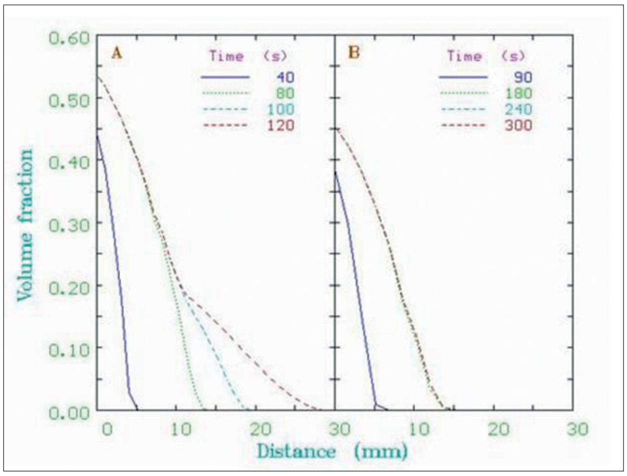

Fig. 8 - Martensite volume fraction as a function of radial distance for different treatment times in: A, 3 inch and B, 5 inch diameter balls.

In figures 7 and 8 it is notable that no increment of martensite fraction occurs at the surface of the balls during equalisation, since the surface temperature during this stage is higher than the temperature at this position at the end of quenching, as figure 2 shows. During the equalisation cooling step, the temperatures of the central zones of the balls reach values below Ms and, as a consequence, at the end of equalisation there is a martensite fraction across almost the whole radius of the 3 inch diameter balls, associated with their radial and circumferential residual stresses. After equalisation the 3 inch balls were stored in boxes to allow them to reach ambient temperature at a very slow cooling rate. This produced the stabilisation and the presence of retained austenite in the balls at ambient temperature.

Using the experimental TTT diagrams and the temperature models obtained, four new thermal treatment processes were tested for the 3 inch diameter balls, consisting of final quenching temperatures of 600, 550, 500 and 450°C at the centre of the balls, over a common equalisation time of 200 s. The aim was create a condition where some bainite percent exists at the centre of the balls after heat treatment, without affecting the surface hardness. Table 3 shows the results of the average surface and central hardness's in the finished balls treated under these conditions.

Tab. 3 - Ball hardness following proposed heat treatments.

Final quenching temperature at the centre of the balls (°C)	Final equalisation temperature of the balls (°C)	Surface hardness (RC)	Central hardness (RC)
600	250	53	45
550	220	57	50
500	203	62	54
450	175	62	62

For final quenching temperatures of 550 and 600°C at the centre of the balls, the surface reached temperatures greater than Ms during equalisation, and tempering occurred. Consequently not enough hardness was obtained at this position. Conversely, at lower central temperatures, (i.e. below 450°C), no austenite transformation occurred above Ms such that high hardness was achieved at the centre of the balls.
However, a quenching time of 55 s (instead of the currently used 80s), resulted in a final central temperature of 500°C (instead of the current 273°C) at the end of the treatment, and maintaining a peripheral temperature at 100°C was found to be adequate. Subsequently, the equalisation for 200s (instead of the currently used 40s), resulted in a uniform ball temperature of 203°C (instead of the current 139°C) at the end of this process.
Figure 9 shows the experimental TTT diagram for the steel of the 3 inch diameter balls. The current and proposed cooling of the central zone during quenching (500°C as the final temperature) and equalization are superimposed.

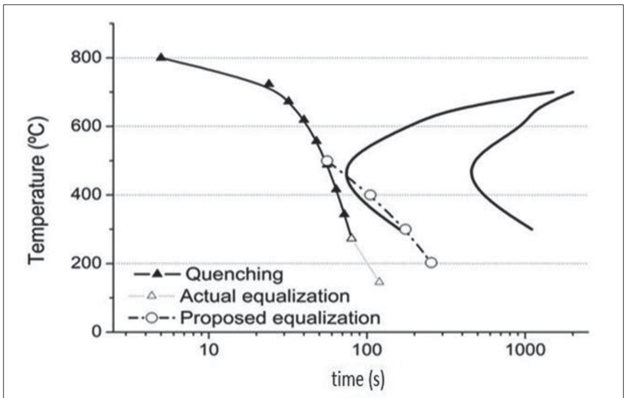

Fig. 9 - TTT diagram for 3inch diameter balls and cooling cycles for the centre of the balls for current and proposed heat treatments

In Figure 9 it can be seen that the centre of the balls currently used does not undergo austenitic transformation at temperatures above Ms. This explains the high hardness in the central zone, in which only martensite and some retained austenite are present. Instead, with the proposed treatment times, some proportion of austenite transforms to bainite at temperatures greater than Ms, which implies a lower hardness in that zone.
After austenisation and thermal treatment of the two balls using the proposed treatment conditions, values of surface hardness 62 RC, volumetric hardness 61 RC and central hardness 53–55 RC were obtained. The volume fraction of each phase present at the centre of the finished ball following the proposed treatment were estimated according to the law of mixtures for the hardness. For typical hardness values of martensite, bainite and austenite of 65, 40 and 22 RC respectively, the volume fractions are: 0.59 martensite, 0.33 bainite and 0.08 retained austenite, compared to 0.93 martensite and 0.07 retained austenite at present. Thus, the above aim was fulfilled.
The results of the Drop Ball tests for the two sets of 20 balls were:

- standard heat treatment: weight loss 0.15%; 5 balls cracked
- proposed heat treatment: weight loss 0.17% ; 2 balls cracked.

The weight loss was similar for both groups of balls, consistent with their comparable surface hardness; however the reduction in the number of fractures specimens from 5 to 2 was remarkable. The superior toughness in the central zone following the proposed treatment was due to lower hardness and lower martensite content at their central zone (volume fraction 0.59 compared with 0.93 currently), which also reduced the residual stresses. In this regard, Figure 10 shows the theoretical circumferential residual stresses following standard equalisation processes [7] and following the proposed heat treatment, as calculated from equations (1) to (3). The stresses are clearly smaller after the proposed process, at their final equalisation temperature of 203°C (standard is 139° C) a smaller volume of martensite formed in the central zone.

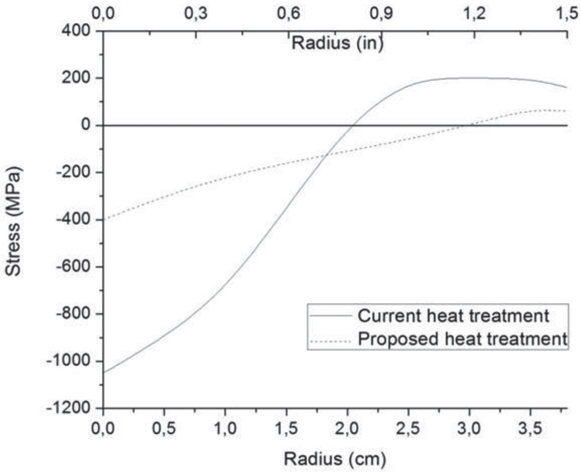

Fig. 10 - Theoretical residual circumferential stresses at the end of equalisation of a 3 inch diameter balls: current (solid line) and proposed (dotted line) heat treatments

CONCLUSIONS

FDM and FEM simulation of the temperature distribution in steel grinding balls during heat treatment has provided the tools for predicting their behaviour during the quenching and equalising processes. The predictions agreed well with measured values and encouraged the search for new heat treatments conditions of the balls, reducing the quenching time and increasing the equalisation time. This improved the quality of the balls by maintaining their peripheral hardness but reducing the hardness of their central zone and thus increasing their toughness.
Specifically, a quenching time of 55s and an equalisation time of 200s resulted in a central zone of 53 to 55 RC hardness (reduced from 61 RC hardness achieved by current heat treatment). At the same time the peripheral hardness was maintained. The number of fractures in Drop Balls testing was 60% lower than for standard balls.

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