RESEARCH PAPER

The Influence of Silicon Addition on Microstructure and Mechanical Properties of Manganese Bronze Alloys

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Received: November 2020 **Revised: January 2021** **Accepted: February 2021**
DOI: 10.22068/ijmse.2063

Abstract: *The present investigation aims to synthesize RB031, RB032 Manganese Bronze alloys equivalent to HTB1 and HTB2 alloys with the addition of silicon and to characterize them with the help of Microstructure and Mechanical properties. The methodology involves melting of alloys in a 300kg coreless medium frequency induction furnace, casting them in Permanent and Shell molds with optimum values of Zinc equivalent and retaining their high mechanical properties. The study includes the development and mechanical property measurements of the alloys synthesized. Characterization has been carried out using optical microscopy and scanning electron microscopy with EDAX analysis for investigation of compositional variations and inquisition of hardness measurement & tensile properties. It is concluded from this work that RB032 alloy cast in Permanent molds has superior hardness and tensile properties compared to Shell molds which far exceeds that of NAB (AB2) alloys processed under similar conditions. Further, this investigation includes grain refinement by suitable Heat treatment studies to combat hot tearing since the strength is adequate enough with RB032 exhibiting higher hardness than other two alloys.*

Keywords: *Zinc equivalent (ZE), Alpha + Beta Phase (α+ β), Hot tearing, Permanent Mold, Shell Mold, Si:Mn ratio, Manganese silicides.*

1. NOMENCLATURE

α: Alpha
β: Beta
γ: Gamma
WZ+WHT: With zirconium with heat treatment
WOZ+WOHT: Without zirconium without heat treatment
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2. INTRODUCTION

Manganese Bronzes are also known as high tensile brasses and high strength yellow brasses special brasses, Manganese brasses on account of their high zinc content. Designers have been selecting Copper base alloys as Bearing materials from times immemorial as the structure is ideal for mating surfaces. Manganese Bronzes were developed mainly for Sea Water Corrosion Resistance applications. These alloys have hardly undergone any change while their use has extended to High Structural Strength Applications. High tensile brass is a complex alloy of Copper and with additions of alloying elements like Al, Mn, Fe, Sn etc. Addition of these elements and others improves its Mechanical properties, Corrosion and Wear resistance to a great extent. The addition of Silicon is generally to improve strength, lubricity and Corrosion resistance of the alloy. Copper and Copper based alloys are the most suitable group of materials as they have good Corrosion resistance and hence extensively used in the construction of Warships. Alloy compositions which combine resistance to the Corrosion conditions encountered in running sea water, suitability of fabrication and reasonable first cost are judiciously selected and specified for the specific components. This investigation is based on the development of Cast Manganese Bronze alloys with Silicon additions as effective alternate materials for the more expensive Nickel Aluminum Bronze and Tin Bronze alloys for potential applications in naval components and systems. Murphy [1] while studying about the effect alloying elements in brasses concludes that the alloying elements increase the strength of brasses and considerably improve their corrosion resistance. These high strength brasses have excellent Casting Characteristics and exceptionally high Mechanical Properties in the Cast condition. In Phase Diagram constructed by Hansen M & Anderko K [2] it is found that up to 32.5% zinc the room temperature phase is alpha (α) which is a solid solution of zinc in Copper. Above 32.5% Zn up to 37% Zn the microstructure consists of alpha (α) and beta (β) phases. Between 39.0 and 56.5%, the structure is usually β', which is the ordered state of β at room temperature. Above 50.0% Zn the brittle gamma (γ) phase appears and renders the alloy very brittle and unfit for industrial applications. These structures are applicable to equilibrium state of cooling and with the solidification obtained in actual casting practice, the various phases appear at lower values especially with the fast cooling process. As more than 3-4 alloying elements are involved recourse in made to the principle of equivalence which is the Zinc Equivalent (ZE) in order to explain structure. The Zinc equivalent is arrived at based on the fact that certain elements behave like Zinc addition. Both HTB1 & HTB2 find applications in highly stressed components at normal temperatures like Marine Propellers and Cones, Condenser Tube Plates, Rudders & Rudder posts, Gun Mountings, hydraulic equipments, Water Turbine equipments, Locomotive axel boxes, Pump Casings, Marine Casings and fittings. Dhar and Biswas [3] in their paper on High Tensile Brass castings and their applications are of the opinion that in the design of Marine Propellers for Coastal and Arctic service, reliability and durability are often more critical consideration than speed and efficiency. The alloy should possess toughness and ductility such that impact loading produces plastic deformation rather than unstable crack propagation and failure of the blade. Better use of their properties of corrosion and cavitations resistance of the high tensile brasses can be made in the design of efficient high speed Propellers.

Thomson [4] in his studies on Charpy impact properties of Bronze propeller alloys discusses that for the Proper understanding of the materials, applications and of their physical properties alone is not considered sufficient in the designing of a ship by a Design Engineer. He should have first-hand knowledge about what salt-water and salty atmosphere will do to his machinery and equipment. The other general point about naval engineering is the great emphasis on reducing weight and space which machinery and systems occupy in warships. There is always pressure to use materials to limit of design stresses, often before this happens in other fields. Sriram [5] in his investigation on High Tensile Brasses stresses on the importance of collision and shock resistance of these materials while designing warships. Microstructure and mechanical properties of Aluminum Bronzes were investigated for influence of heat treatment by Peter Slama et. al [6], and are of the opinion that the vital part of the Naval designers business is with the help of a Metallurgist to recognize, adapt for Naval purposes and exploit the growing field of materials available today for the benefit of future ships. The selection of materials for Marine application such as Ship Construction, Desalination Plants and so forth is governed by surrounding corrosive environments which may include salt water, fresh water, or various corrosive cargoes such as oils, chemicals and so on [7].

In the design of Marine Propellers used for coastal and arctic service, Arthur H Tuthill [7] has stated that reliability and durability are often more critical consideration than speed and efficiency. The alloy used should possess toughness and ductility such that impact loading produces plastic deformation rather than unstable crack propagation and failure of the blade. Better use of the properties of Copper alloys like Corrosion and cavitation resistance may be made use of in the design of high speed efficient high speed propellers. High strength yellow brasses also known as high tensile brass or Manganese Bronze have very high potential to replace more expensive tin bronzes and Aluminum bronzes for various applications such as bearings and structural parts. Dhar and Biswas [3] in their paper on high tensile brass castings clearly specify that the effect of alloying is to considerably increase the strength and Corrosion resistance. The two groups of High Tensile Brass alloys show Duplex alpha (α) plus beta (β) [(α+ β)] structure and beta (β) in the microstructure with Iron rich compounds, the amount of beta β increase with increase in Zn content.

Hamid doorstonohammadi, Hamid Moridsham [8] investigated the properties of $Cu_{60}Zn_{40}$ alloy and the effect of Silicon on the microstructure and ordering behavior of this alloy. They found that presence of silicon helps formation of beta phase and there was change from duplex alpha + beta to single beta phase in the alloy. Increase of ordering temperature was noticed by dilatometric analysis. Also they found the usefulness of this alloy as an alternative to free cutting leaded brass based on their properties.

While discussing the microstructure of High Tensile strength brasses containing Silicon and Manganese, Sun, et. al [9] concluded for the alloys C67300, C67400 (Cu-35%Zn, 2.5%Mn - 1.0% Si-1.5%Al) and (Cu-35%Zn, 2.5%Mn - 1.0% Si) that their cast structures consisted of copper rich FCC α-Phase, ordered β phase and Mn_5Si_3 distributed uniformly in C67300 alloy and concentrated at the β boundaries in C67400 alloy. Quenching the alloys from a temperature near the solidus and further tempering them between 400-500°C transforms all β' to α-Phase in C67300 alloy and in C67400 alloy the α-Phase precipitates on the beta boundaries and shows a Widmanstaten structure. From the extensive survey of literature it is evident that for consistent properties in Manganese Bronzes with Silicon additions, the Si:Mn ratio must be held in a range where it is known by examination that the desired physical properties are obtained. Different Silicides in varying combination would certainly cause altered physical properties in the alloy. The ratio of Silicon to manganese is critical to form the correct Manganese Silicide intermetallic compound to achieve the required mechanical properties. Addition of Silicon significantly influences microstructure and properties of Manganese Bronze alloys.

This investigation focuses on synthesizing RB031 & RB032 alloys which are unique compositions by themselves, Manganese Bronzes (High Tensile Brasses) approximately corresponding to specification BS1400 HTB1 & HTB2, and ASTM 505, B505 B22, CDA 86500, C86300, DIN En1982 CC763, CC7625 and compare their Mechanical properties with NAB(AB2) alloy. An earnest attempt has been made here to develop cast Manganese Bronze alloys with Silicon as an effective alternate for the more expensive Nickle Aluminum Bronze and Tin Bronze alloys.

3. EXPERIMENTAL PROCEDURE

The Melting of High Tensile Brasses or Manganese Bronzes with Silicon addition was carried out in coreless medium frequency induction furnace as per production procedures followed with brasses and nickel aluminum bronze alloys. Optical OLYMPUS microscope BX51N1 using ClemexImage Analyzer was employed for microstructural studies. ASTM148-1978 specifications were followed for tensile strength measurements. Heat treatment of the castings was carried out in a AFML make resistance furnace with range up to 1200°C, accuracy ±5°C. The alloys developed meet the following requirements. The etchant used for obtaining the microstructures of RB031, RB032 and NAB (AB2) alloys has been $NH_4OH + H_2O_2$ and the magnification used was 200X. Hardness value were measured using microharness tester as per ASTM E348.

The alloys were melted at 980°C in a coreless induction furnace of 300 kg capacity, power: 175KW, Make: inducto-therm, Lining material: Alumina Ramming mass, Crucible: silicon carbide.

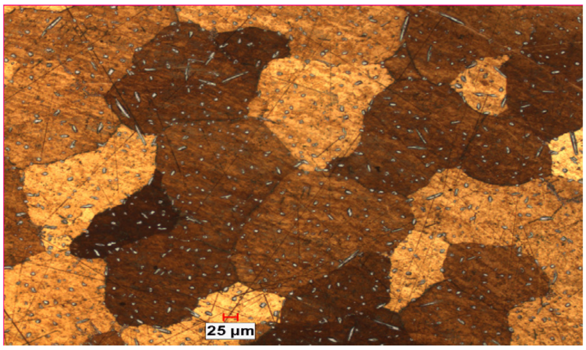
Table 1. Chemical composition of the alloys

RB032		**NAB(AB2)**		**RB031**	
Element	**Actual**	**Element**	**Actual**	**Element**	**Actual**
Cu	63	Cu	82	Cu	59.3
ApZn	62.5	Al	8.65	APZn	54.4
ZE	49.83	Fe	4.04	Ze	47.86
Zn	22.1	Ni	3.92	Zn	34.85
Al	4.83	Zn	0.236	Mn	2.81
Fe	3.43	Sn	0.213	Al	1.66
Mn	2.73	Sb	0.152	Si	0.78
Ni	2.42	Si	0.105	Sn	0.121
Si	0.98	Pb	0.062	Fe	0.087
Sb	0.074	Cr	0.061	Sb	0.057
Pb	0.051	Mn	0.049	Pb	0.047
Sn	0.046	Bi	0.014	Co	0.025
Co	0.04	Zr	0.011	Zr	0.016
S	0.007	S	0.006	Ni	0.014
Zr	0.011	P	0.005	S	0.009
		Mg	0.003		
		Be	0		

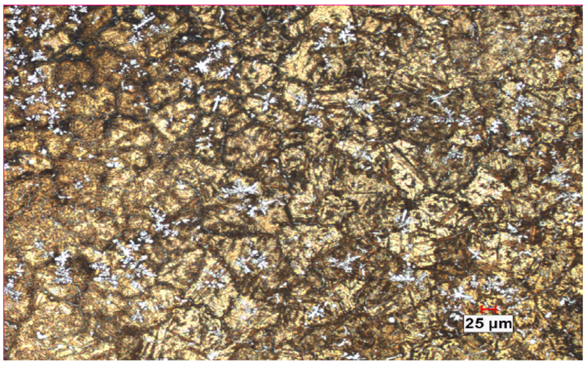
4. RESULTS AND DISCUSSION

4.1. Microstructure

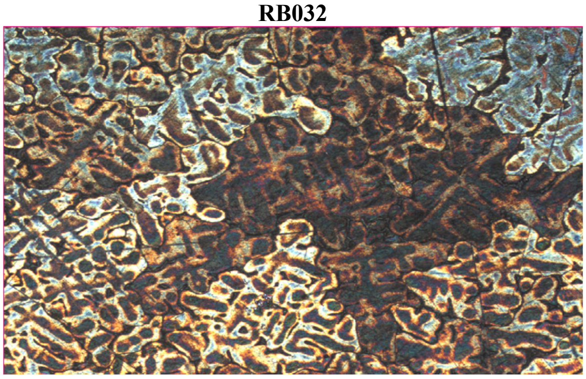
Figure 1(a) & (b) depicts Optical Micrographs of RB031, RB032 and NAB alloys under Shell mold and Permanent mold conditions. From the micrographs, it is inferred that Mn_5Si_3 precipitate is formed during quenching. This precipitate is formed in both RB031 & RB032 alloys upon quenching near the solidus temperature. On further tempering the quenched alloy between 400°C-500°C indicates that β' phase transforms to α in one alloy, while in other the α precipitates at β boundaries and shows a Widmanstatten morphology.



RB031

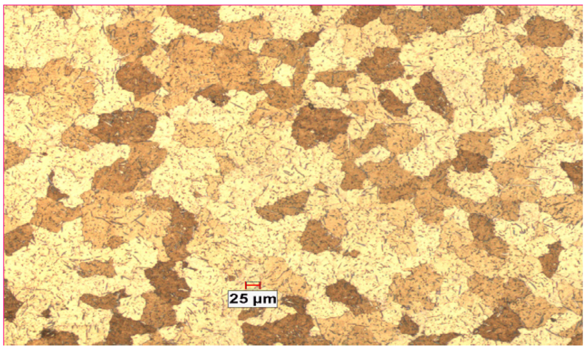


RB032

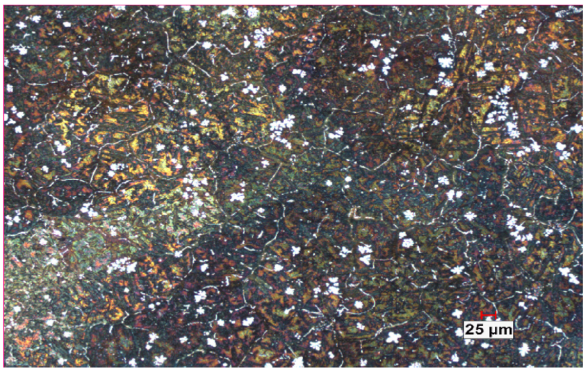


NAB(AB2)

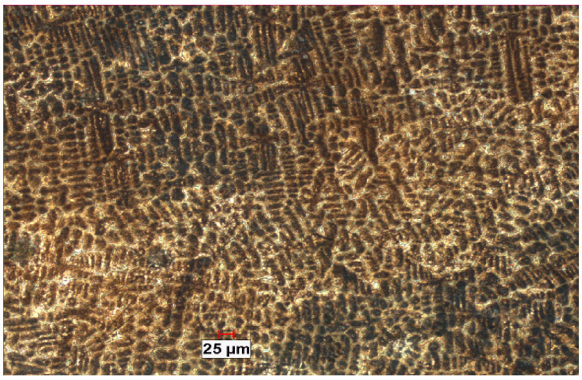
Fig. 1. (a): Microcrographs of alloys under Shell mould condiion



RB031



RB032



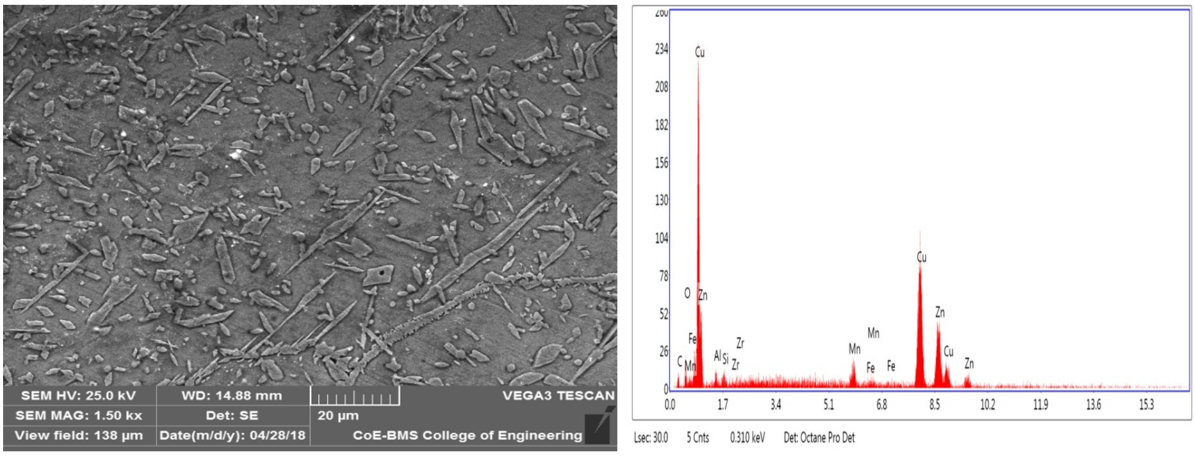
NAB(AB2)

Fig. 1. (b): Microcrographs of alloys under Permanent mould condition

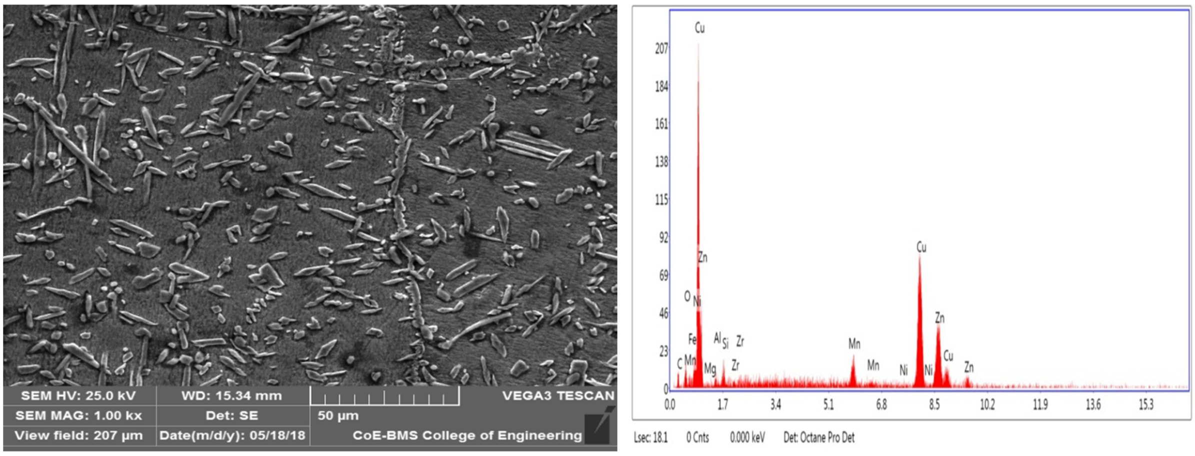
Heat treatment of alloys was carried out by holding the alloys for 60 min at 720°C and quenching in water with aging temperature of 330°C for 2 hours and air cooling.

Figure. 2 (a & b) Shows the scanning Electron micrograph of RB031, RB032 alloys under Shell mold and Permanent mold conditions and their corresponding EDAX pattern. It is noticed that as the Zinc Content increases significantly over 32.5%, the α crystals can't hold all the Zinc atoms in solid solution, instead as the alloy freezes, a new crystal phase solidifies. This β phase can hold up to 55% Zinc in solid solution, just under the freezing point. Alloys from 45.5- 50% Zn will freeze and remain 100% β unti1 450°C when β

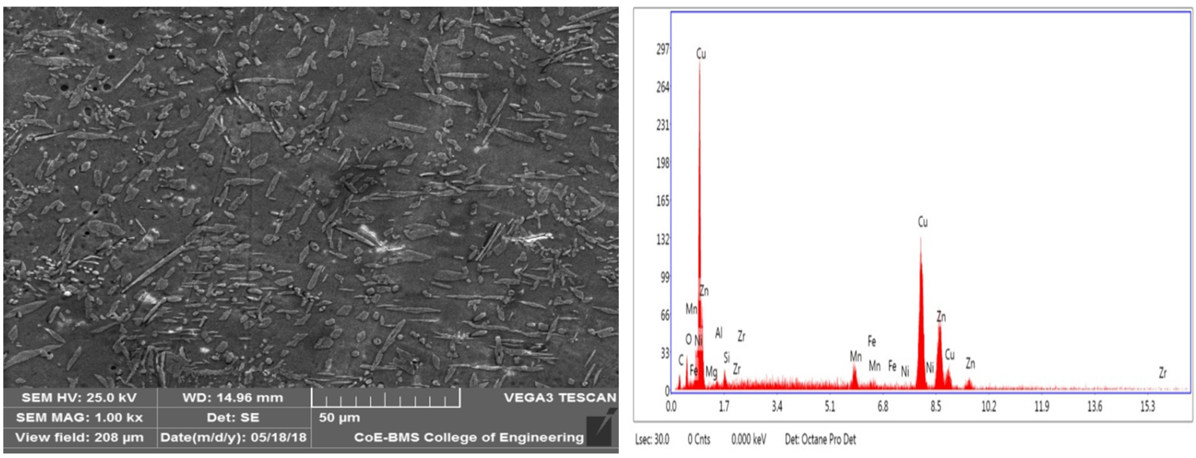
[DOI: 10.22068/ijmse.2063]



RB031



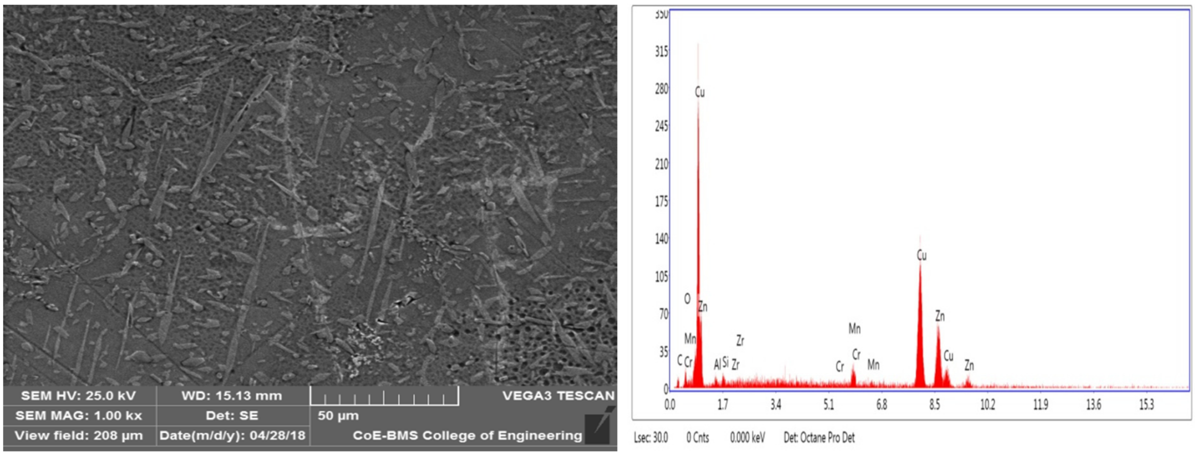
RB032



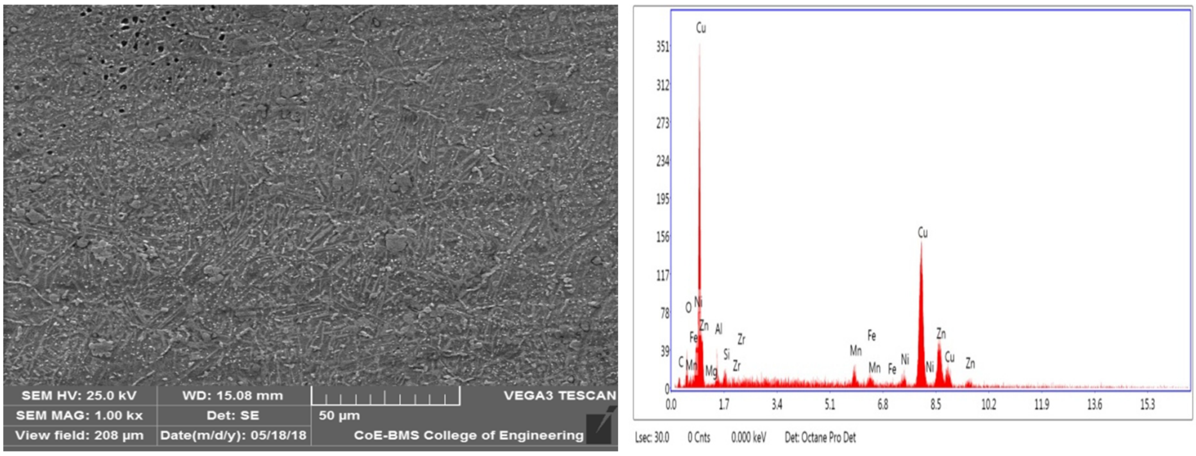
NAB(AB2)

Fig. 2. (a): SEM Micrographs of alloys under Shell mould condition

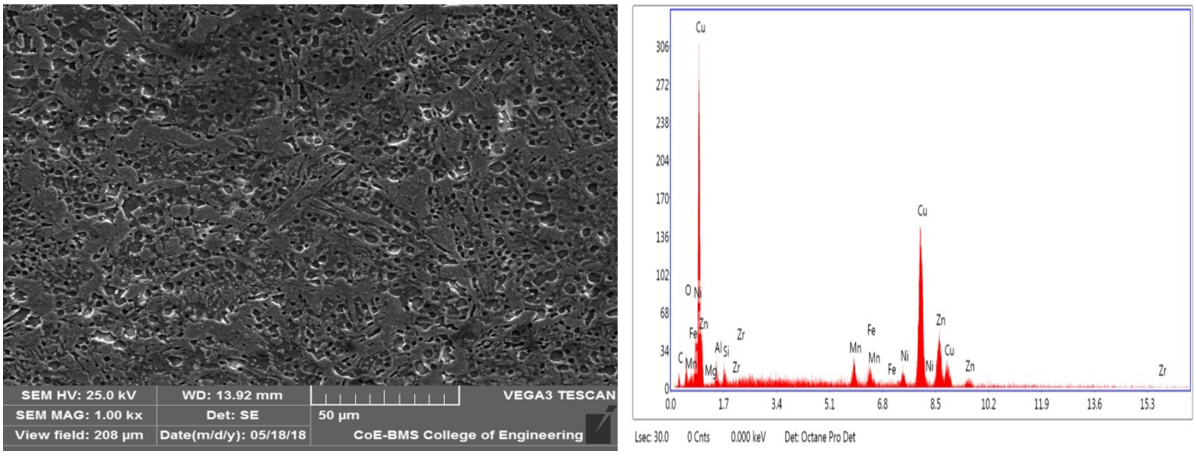
[DOI: 10.22068/ijmse.2063]



RB031



RB032



NAB(AB2)

Fig. 2. (b): SEM Micrographs of alloys under Permanent mould condition

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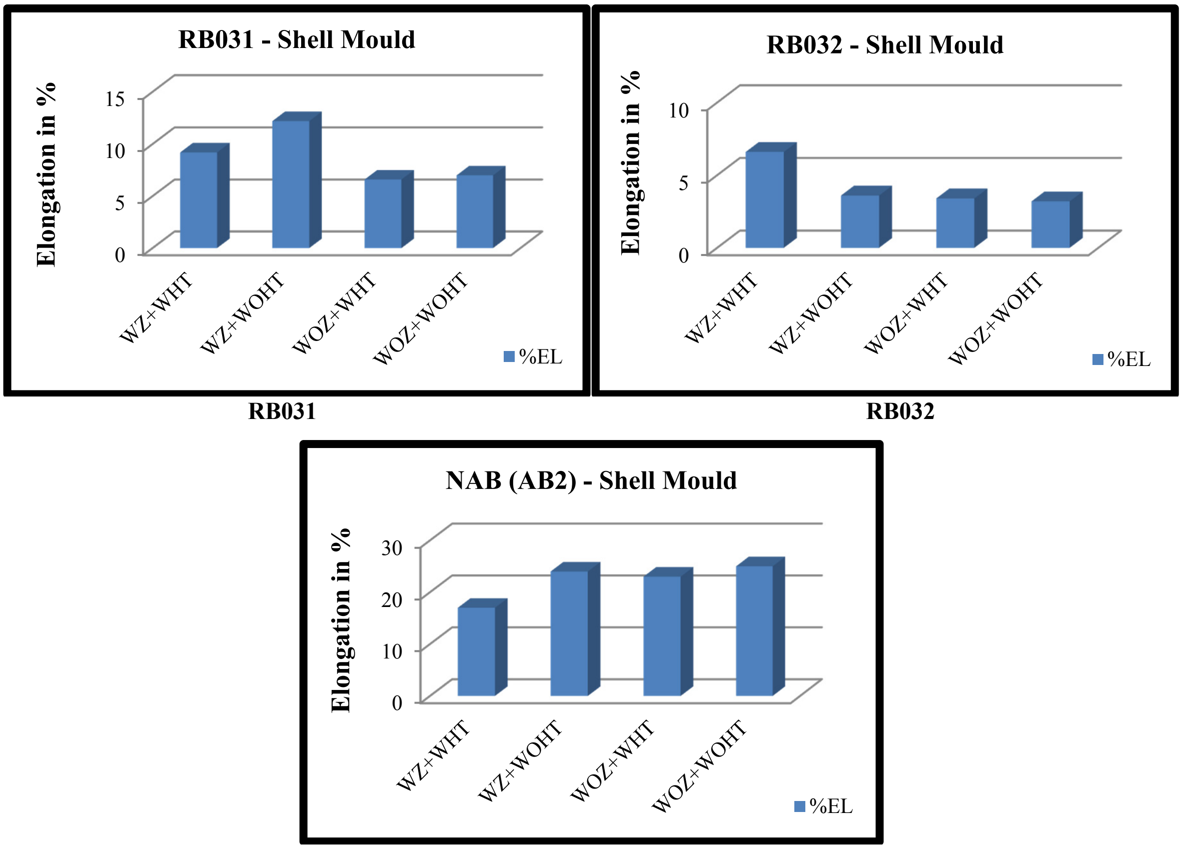
changes to β' an ordered phase. The β phase is strong but quite brittle as the Zinc content increases over 49%. Between 39% and 45.5% Zn the β as it cools, will develop a crystals at grain boundaries. This field is the two phase α-β regions where castings will show increasing amount of β. As the Zinc increases the strengths of the alloy will also increase. It is noticed that α is relatively soft with high ductility and the β is relatively strong with lower ductility. The presence of β crystals strengthens the alloys by resistance to deformation. The Shell cast structure shows Manganese silicide is in the form of fine needle shaped particles in a Coarse grained β phase. The 47.6% ZE has resulted in the room temperature β phase and the relatively slow cooling in Shell molds is reflected by the coarseness of the β grains. Very fine Manganese Silicide needles in a uniformly fine grained β matrix is the reason for higher mechanical properties in permanent molded samples of RB032 alloy. Permanent molding leads to very fast solidification which results in fine grain structure. Microstructural analysis of NAB (AB2) alloy shows fine stable reinforcing Kappa phase.

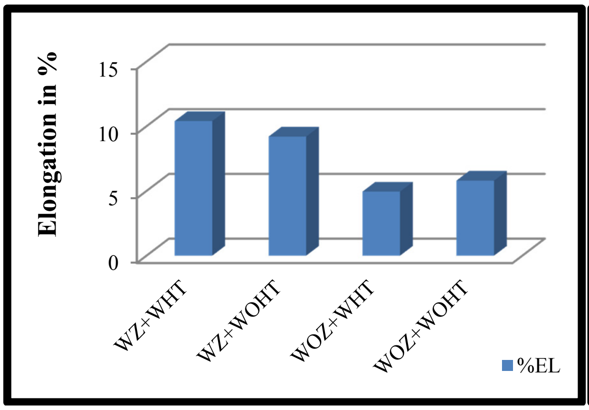
4.2. Tensile Properties

Figure 3 (a & b) shows the variation of ductility, Figure 4 (a & b) shows the variation tensile strength of RB031, RB032 and NAB(AB2) alloys under Shell molding and Permanent molding conditions respectively. It is observed from the graphs that both RB031 and RB032 exhibited higher tensile strength when compared with NAB alloy. Among all three alloys studied, RB032 demonstrated superior tensile Characteristics when evaluated with RB301 and NAB alloy.
It is observed that addition of zirconium has significantly improved the Ultimate Tensile strength and Yield strength in both RB031 and RB032 alloys. Quenching and subsequent aging of the sample during heat treatment has led to martensitic structure β which has resulted in increased strength of the material in a permanent molded casting. In case of NAB (AB2) alloy the presence of kappa phase has resulted in increased strength levels and reduction in elongation. Slow cooling in shell molding is seen in coursnes of beta grains and lower mechanical properties.

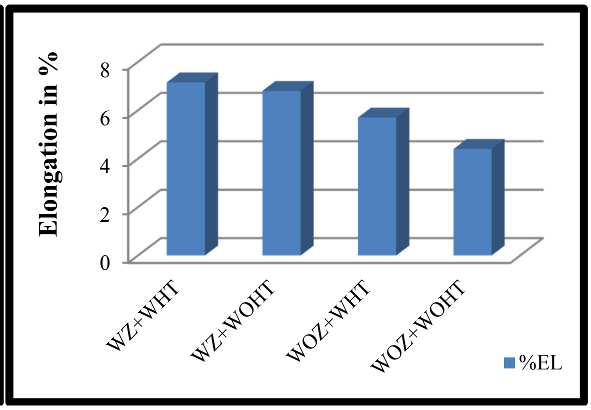


NAB(AB)

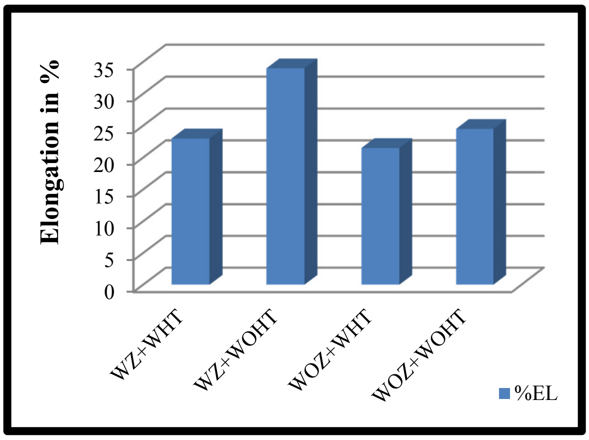
Fig. 3. (a): Variation of ductility of alloys under shell molding condition



RB031



RB032



NAB(AB)

Fig. 3. (b): Variation of ductility of alloys under permanent molding condition

The Tensile strength and yield strength in these alloys, increase with Zn Equivalent and reach a maximum in the presence of increasing β phase and later drops with the appearance of γ phase.

The percentage elongation decreases with increase in Zinc Equivalent and the trend shows that this can be lower than the specification value if the ZE is 55.67% and this is due to the presence of γ phase in the structure. From all this it is to be inferred that ZE value is critical for obtaining a suitable microstructure and hence mechanical properties.

In the microstructures of RB031 and RB032 alloys it is found that there is a uniform distribution of intermetallic Manganese Sillicides in a fine grained matrix of α+β phases. In the case of RB31 alloy some problems of shrinkage and pipe formation were noticed during casting stage and the strength levels are considerably lower.

This investigation has revealed that keeping the alloy at 750°C for 1 hour will develop an approximate 20% α and 80% β microstructure. This is being followed by cold water quench to stop further α formation. After the quench a further heat treatment is done to strengthen the β phase. Holding the alloys at 350°C for 2 hours will cause the Copper atoms in the β phase to change from random distribution to zones of an "ordered phase", where the atoms are arranged in a repeatable pattern that inhibits the deformation by slip.

It is seen from the graph that the % difference in yield strength among RB031, RB032 is 3.52% in Shell mold condition and 16.32% in Permanent mold condition; whereas the % difference in yield strength among RB032, NAB is 15.3% in Shell mold condition and 38.7% in Permanent mold condition. Thus indicating the superiority of RB032 alloy in Permanent mold condition when compared with other two alloys.

[DOI: 10.22068/ijmse.2063]

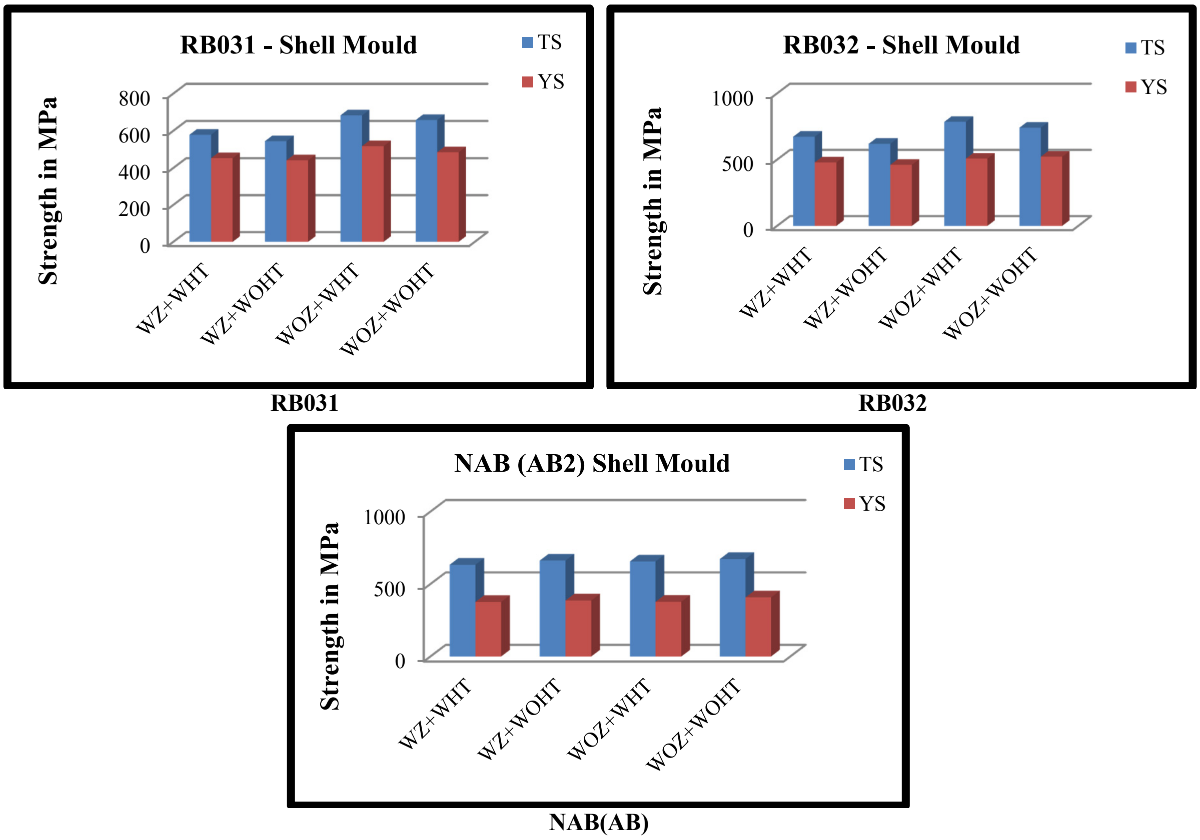


Fig. 4. (a): Variation of strength of alloys under shell molding condition

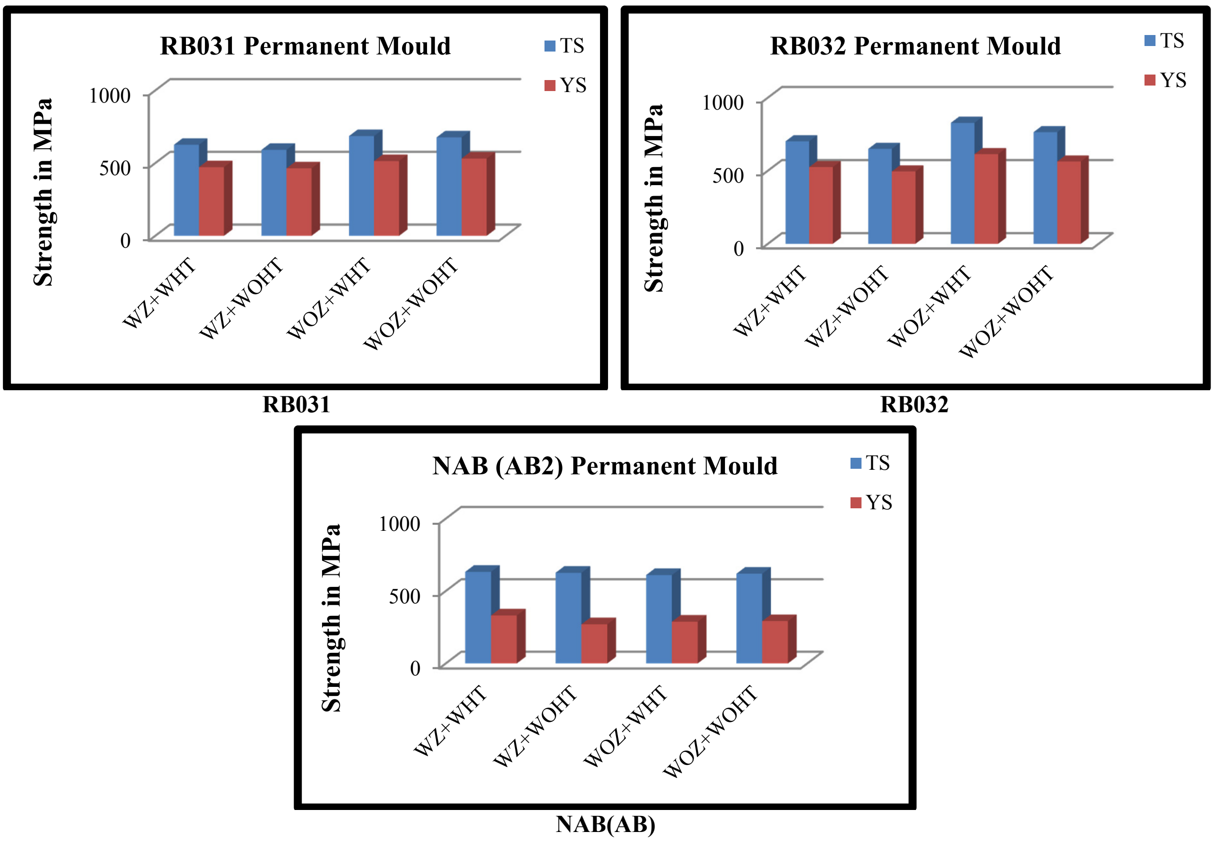


Fig. 4. (b): Variation of strength of alloys under permanent molding condition

4.3. Hardness

Figure. 5 presents the variation of hardness values of RB031, RB032 and NAB alloy in permanent and shell molding conditions. It can be seen from the graph that 12.18% difference in hardness value between RB031 and RB032 in permanent mold condition, 7.25% in shell mold condition and 7.96% difference between RB032 and NAB(AB2) alloy in permanent mold condition, 3.67% in shell mold condition. Indicating higher strength in RB032 alloy when compared to other two alloys. As discussed in the previous section, the rapid cooling rate in the permanent mold yields in finer grain size whereas in case of shell molding, the slow cooling rate is seen in coarse beta grains and lowers the hardness of the alloy. Finer the grain size, higher will be the hardness of the alloys.

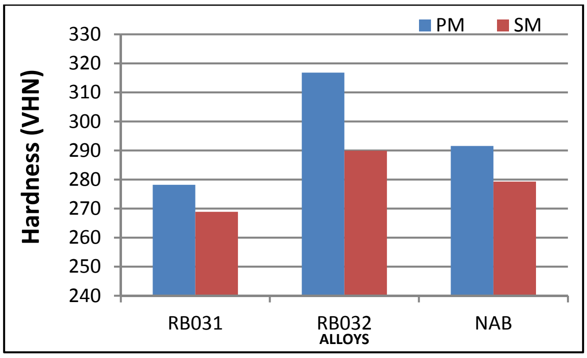


Fig. 5. Microhardness comparison graph

5. CONCLUSIONS

1. The present investigation indicates that optimum values of ZE results in an optimum microstructure, yet retaining high mechanical properties is possible in the alloy RB032 and this is truer with permanent molded castings than with shell molded castings.
2. Permanent molded castings of RB032 alloy have exhibited superior mechanical properties than Shell molded castings in all the Characterization.
3. RB032 alloys exhibited better hardness than the other two alloys with 12.18% higher hardness than RB031 and 7.96% than NAB (AB2) in the permanent mold condition.
4. Yield strength of RB032 alloy in Permanent mold condition is superior to other two alloys.
5. Overall, the tensile strength and yield strength increase with zinc equivalent content and reach a maximum in the presence of increased β phase and later drop with the appearance of ϒ phase. The elongation decreases with increase in ZE%.
6. With its better mechanical properties & all other characteristics, the RB032 alloy will be an effective and more economical substitute than NAB (AB2) alloy.

6. ACKNOWLEDGMENT

The results presented in this paper are under the Project “Synthesis and Characterization of High Strength Manganese Bronzes with Silicon addition” funded by the Science and Engineering Research Board (SERB) – Government of India New Delhi, and M/S RAPSRI Engineering Products Limited, Harohalli, Kanakapura Taluk, Ramanagara Dist., Karnataka State under Industry– Institute interaction with a grant of Rs. 34.0 lakhs for a period of three years. Authors would like to express their deep sense of gratitude to both the agencies for their kind gesture in releasing the funds. Further, authors would like to thank Dr. C.P.S Prakash, Principal DSCE for his unstinted support and encouragement during the course of this investigation.

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[DOI: 10.22068/ijmse.2063]