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The Progress of High Performance Sintered (Ce,Nd)-Fe-B Magnets Technology

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Abstract:

Sintered Nd-Fe-B magnet is widely used for its excellent magnet property. At present,the substitution of Nd with high-abundance Ce has become a research focus for its cost advantage.This paper will introduce the intrinsic property of (Nd,Ce) -Fe-B permanent magnets;phase changes and composition of magnets after the substitution treatment; the impact of element addition and parameter optimization on magnetic phases and micro-structure regulation.The micro-structure and magnetic property of sintered Nd-Fe-B magnets by double main phase method are mainly introduced. And study on magnetic property and corrosion resistance of different content of cerium is highlighted.

***Keywords**: Microstructure, Cerium, dual main phase, magnetic property.*

I. INTRODUCTION

Up until now, sintered Nd-Fe-B magnets has been considered as magnets with the highest magnetic properties with a theoretical maximum energy product$(BH)_{max}$ up to $512kj/m^3$. Its excellent magnetic property is the key to small sized and light weight applications. It is also been widely applied to applications made of rare earth permanent magnets,such as motors, wind turbines,smart wearing, new-energy vehicles and railway transportation. In recent years, China has become a major part of the mass production of rare earth permanent magnets worldwide. In 2018, the global demand for sintered Nd-Fe-B magnet reached 180,000 tons, with China accounting for more than 85% of that. Therefore,China plays a prominent role in the industrial chain of sintered Nd-Fe-B magnets, especially in property and raw material.

Now, with the remarkable growth of global capacity of sintered Nd-Fe-B magnets, unrenewable resources of prominent importance such as Nd, Pr, Dy, and Tb have become global critical resources. Therefore, reducing Nd consumption is a key approach to the sustainable development of sintered Nd-Fe-B magnets industry. In the process of exploiting Nd, high abundance Ce, carried by Nd, is collected for its less of demand.With tenth price of Nd, but ten times storage of Nd, Ce is widely used in Nd-Fe-B magnets, producing magnets with high performance. In this paper, intrinsic magnetic property of $Ce_2Fe_{14}B$, phase possibilities,elements distribution, and technological design in production process will be analyzed. In addition, some research achievements, including property and corrosion resistance of magnets with different content of Ce will be compared and summarized. All-above mentioned are expected to promote

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the development sintered (Ce,Nd)-Fe-B magnets and the substitution of Nd with Y and La.

II. THE INTRINSIC PROPERTY COMPARISON BETWEEN $CE_2FE_{14}B$ AND $ND_2FE_{14}B$

The outer layer's valence state of of two neighboring atoms Ce and Nd are $4f^15d^16s^2$ and $4f^46s^2$ respectively, and the stable valence state of Ce in rare earth oxide is +3 or +4,but Nd is +3 only. In $Nd_2Fe_{14}B$ phases, Nd is +3, and the strong electrons coupling between 4f layer of Nd and 3d layer of Fe exhibits a high magnetocrystalline anisotropy field, which is 5840kA/m, with a corresponding saturation magnetization 1.6T. In $Ce_2Fe_{14}B$ phases, Ce has the valence of Ce^{3+} and Ce^{4+} simultaneously, Ce^{3+} contains a 4f electron with a 2.24 μB^+ magnetic moment; Ce^{4+} contains no 4f electrons, so its magnetic moment is 0 μB^+. By calculation(table 1), we can learn that the average valence of Ce is +3.44, indicating that Ce^{+4} can reduce the saturation magnetization(Ms) and magnetocrystalline anisotropy(K) of $Ce_2Fe_{14}B$ to 1.17T and 2080kA/m respectively. Recent years, researchers have discovered that controlling space environment of Ce can change its valance state and magnetic property ,so as to further improve the magnetic property of Nd-Fe-B magnets;Ce tends to be Ce^{+3} with additional Ga ;And Ce is also Ce^{+3} when the substitution is at 20-40wt% .To sum up, the saturation magnetization of $Ce_2Fe_{14}B$ is 0.7 times higher than that of $Nd_2Fe_{14}B$, and its magnetocrystalline anisotropy field is 0.5 times lower than that of $Nd_2Fe_{14}B$. Therefore, substitution or addition of other elements can be effective to improve magnetic property; In addition, the substitution of Nd with Ce is a feasible way to produce resource-conserving rare earth permanent magnets with high commercial interests.

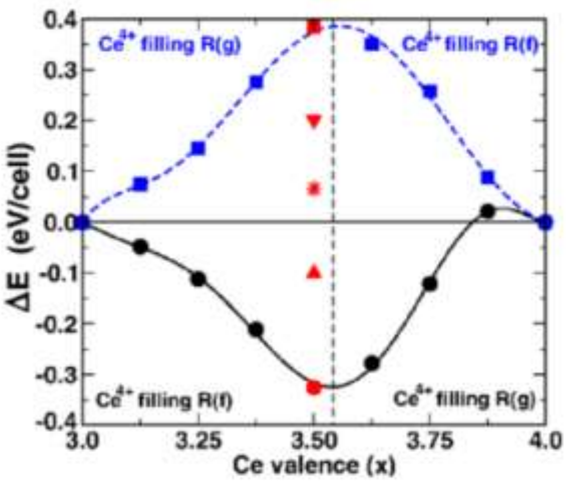

Fig 1 The mixed valence state of Ce in the $Ce_2Fe_{14}B$

III. PHASES OF SINTERED (CE, ND)-FE-B MAGNETS AND MICRO-STRUCTURE OF STRIP CASTING MATERIALS

The structure of $Ce_2Fe_{14}B$ phase is stable and hard to decompose, but in the producing process, in order to produce anisotropic magnetic crystal phases, the raw materials need to be cooled down to room

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temperature after the high temperature melting process.We can see from table 2 that $Ce_{13}Fe_{82}B_5$ is in the junction area of $CeFe_2$, $Ce_2Fe_{14}B$, and Ce_2Fe_{17},demonstrating it is composed by these three materials and high-melting point α-Fe during the solidification.In the producing process of sintered Nd-Fe-B magnets, we can restrain the growth of α-Fe by strip casting materials； control the nucleation rate of strip casting material by annealing temperature;regulate columnar crystal growth and the distribution of RE-rich phases by the conduction rate.The research focus on Ce-containing strip casting material is full or partial Ce substitution.

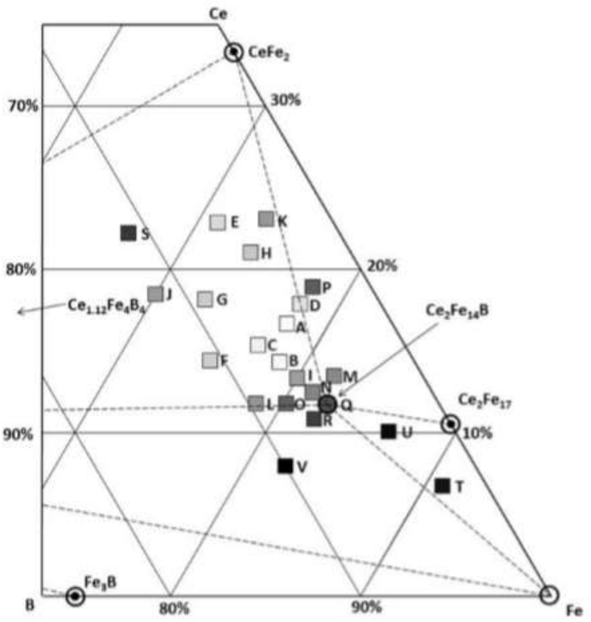

Fig. 2 Section of the Ce-Fe-B phase diagram

With Ce being the only RE element and a 1.8m/s rolling rate ,$Ce_{30.5}Fe_{bal}B_1$(wt.%) strip casting material material has an even micro-structure due to its varied phases, such as $Ce_2Fe_{14}B$, Fe_2B, $CeFe_2$,and α-Fe.However, when Ho/Nd element and a small amount of Mn are added, and B element is properly decreased, the micro-structure of strip casting is promoted because RE-rich phases along columnar crystal spread evenly,the percentage of hard magnetic phases of $Re_2Fe_{14}B$ is significantly increased,as well as other orientation degrees.The micro-structure of strip casting materials with different content of Ce substitution(table 3) demonstrates that with an increase of Ce substitution, columnar crystal tend to become wider.When the substitution accounts for 56wt.% of all the rare earth, gain boundary phases and magnetic phases pile on separately. This phenomenon indicates that during the producing process of Ce-containing magnets, we should take the formation of phases in strip casting materials into consideration,and be aware of the nucleation sites around rolling areas and the growth of columnar crystal affected by the decrease of thermal conduction quotient of alloy fluids.The micro-structure of Ce-free and Ce substitution(50wt.%)strip casting materials(table 4) shows that Ce-containing strip casting material doesn't contain α-Fe phase,because its thickness of the majority phase $RE_2Fe_{14}B$ is 3-5μm,and the thickness of

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RE-rich phase is 0.2-0.3μm, meaning it is beneficial for making grains with the same size and is qualified for manufacturing magnets with high performance.

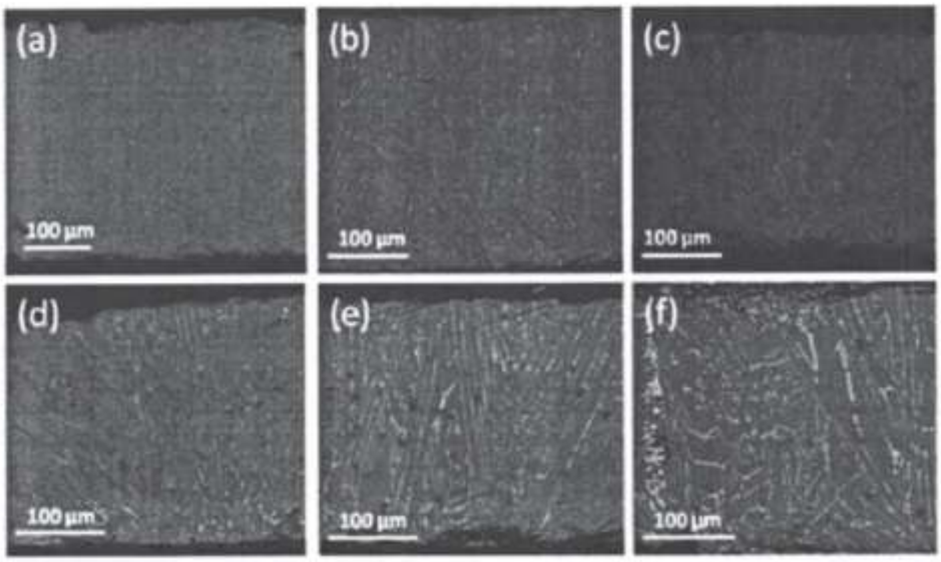

Fig.3 The microstructure of [(Pr, Nd)1-xCex]27 5Dy3FebalAl0.1Cu0.1B1 (wt. %, x=0, 0.08, 0.16, 0.24, 0.32, 0.56) strip-casting flakes

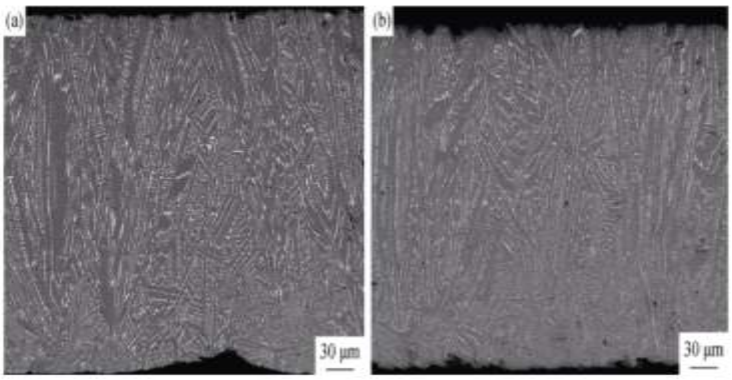

Fig. 4 Cross-sectional BSE images of the strip-cast flakes (a) Nd30FebalB1 and (b) Nd15Ce15FebalB1

IV. DOUBLE MAIN PHASES TECHNOLOGY

To further improve the coercivity of sintered Ce Mgnets, the Double Main Phases(DMP) technology is suggested.The theoretical basis for DMP is forming a phases-interval micro-structure with different component through the interaction of magnetostatic energy to stop the magnetic reverse of phases of small magnetocystalline anisotropy with phases of bigger magnetocystalline anisotripy, so as to improve the coercivity of magnets. There are 3 kinds of phase possibilities(table 5) of magnets with double main phases from the perspective structure:The first one(5a) is Nd-Fe-B grains with bigger magnetocrystalline

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anisotropy and(Ce,Nd)-Fe-B grains with small magnetocrystalline anisotropy distribute at an interval order;The second one(5b) is high-melting point,small sized Nd-Fe-B grains swallowed by bigger sized (Ce,Nd)-Fe-B grains during sintering process;The third possibility(5c) is one of the magnetic phases acts as the fluid phase in annealing or sintering process,forming a grid structure.5a magnets can achieve a high coercivity.

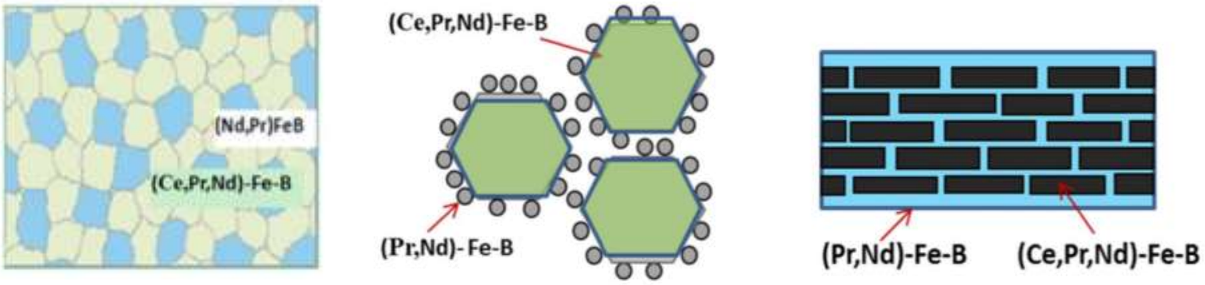
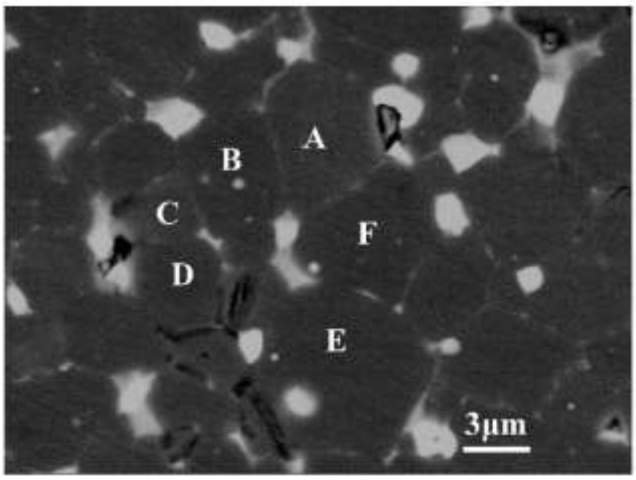


Fig.5 Schematic diagram of dual main phase magnet

Double major phases Ce magnets technology is to produce magnets by mixing the high-content Ce strip casting material and Ce-free strip casting material at a specific proportion with powder metallurgy technology.Because the melting point of Ce is lower than Nd,the technology in natural aging needs to be redesigned.The technology of Ce-containing magnets is different from others because its sintering temperature is lower than Nd-Fe-B magnets, and its annealing process is simplified to one time low-temperature annealing, different from the traditional two times. As a result, double major phases technology can shorten the production cycle of magnets and lower energy consumption, which is good for cost reduction.Using scanning electron microscope to analyse the micro-structure and component of magnets producing by this technology(table 6), researchers find that the micro-structure of double major phases magnets is identical to 5(a) .



main phase grains	Nd	Ce
A	30.32	0.85
B	13.44	16.50
C	15.97	14.24
D	15.87	14.49
E	28.05	3.90
F	17.50	12.00

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Fig. 6 BSE image and the compositions of matrix grains of Ce9Nd21FebalB1M magnets

V. PROPERTY AND CORROSION RESISTANCE OF SINTERED CE MAGNETS

Mixing 50wt%(Ce/RE) Ce-containing strip casting material with Ce-free strip casting material at a specific proportion,the magnetic property of magnets with different content of Ce-subs5itution is different(table 7),and for that reason the Br curve is not liner.When Ce substitution is between 10-30wt%,Br shows a small difference;when Ce-containing strip casting material is at 50wt%(Ce/RE) ,the Br curve shows a steep slope,which may attributed to Ce^{+3} which is subject to low content of Ce;when Ce substitution is at 20wt%, the H_{cj} of magnet presents an unusual growth.To sum up,when Ce substitution is less than 30%wt,(BH)max can exceed 40MGOe, which can meet the requirement of the middle-profile market of magnetic applications.

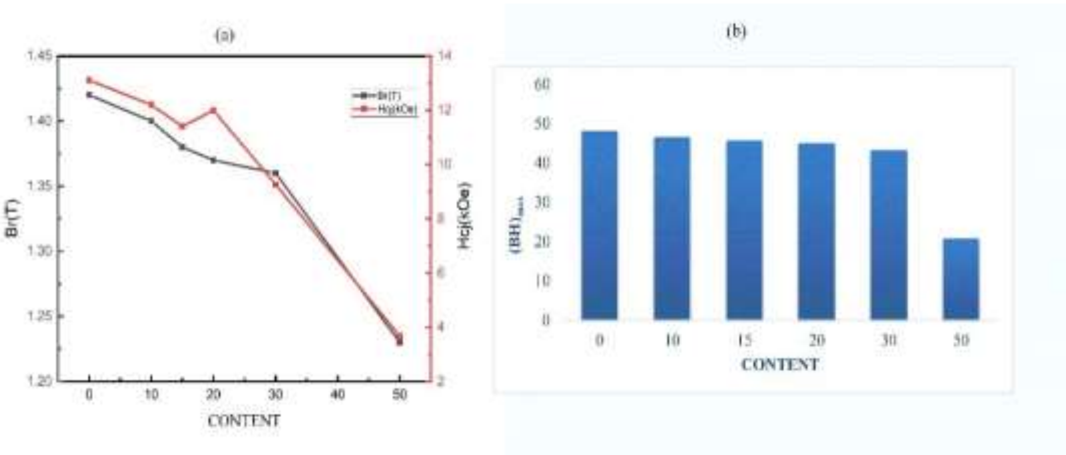

Fig.7 The corresponding Br, Hcj (a) and (BH)max (b) with different Ce content

When Ce substitution is at 20wt%, researchers compared the magnetic property and corrosion resistance of magnets with single and double main phases,and the corrosion resistance of Ce-containing magnets and commercial magnets(table 8).The Br and Hcj of DMP magnets are both higher than that of SMP magnets(8a).This paper compares the corrosion resistance of SMP magnets with DMP and multiple main phases magnets, and i_{corr},$1/R_{ct}$, and mass loss are parameters to show the difference between them.

We can see, from the table, that when y＞1, the property and corrosion resistance of DMP magnets or multiple main phases magnets are better than that of SMP magnets. 8c shows that (BH)max can reach 45MGOe, when Ce substitution is at 15wt%,and the mass loss situation of N45(BHmax=45MGOe)and N33(BHmax=33MGOe)after

corrosion.It demonstrates that the corrosion resistance of 15wt% Ce-containing magnets is comparable to that of N45 commercial magnets, better than N33. In conclusion,stable structure of DMP Ce magnets can meet the requirement of magnetic applications.

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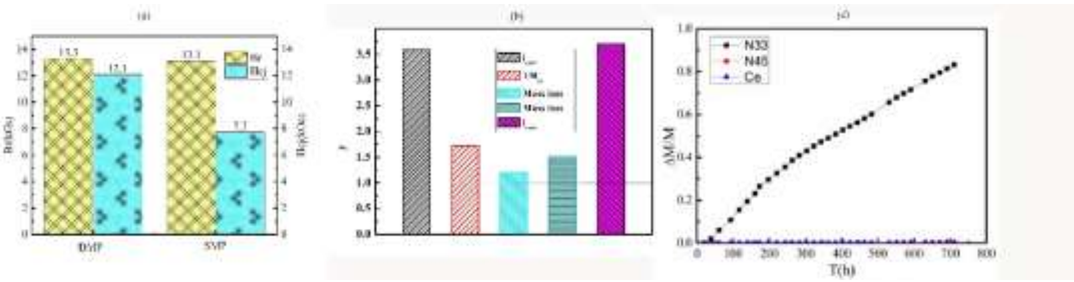

Fig. 8 Comparison of magnetic properties (a), corrosion resistance (b) of single and dual main phase magnets and corrosion resistance between Ce magnets and commercial magnets

SUMMARY

Putting high-abundance LRE Ce element in sintered Nd-Fe-B magnets can improve the efficient use of RE resources significantly,which is compatible to environment-friendly and resource-reserving development path.Analyzing from the perspective of intrinsic magnetic property, the magnetocrystalline anisotropy of $Ce_2Fe_{14}B$ is lower than $Nd_2Fe_{14}B$;with DMP technology,phases with higher magnetocrystalline anisotropy can stop the magnetic reverse of phases with small magnetocrystalline anisotropy, so as to improve the Hcj of magnets. In addition,phases such as $CeFe_2$ and Ce_2Fe_{17} are easy to appear in the producing process of Ce-containing magnets,so adding elements such as Mn,Ho,and B and controlling the cooling rate are necessary to restrain the emergence of non-permatent phases.Commercial sintered (Ce,Nd)-Fe-B magnets can be made by mixing 50wt% Ce substitution strip casting material with Ce-free strip casting material at a specific proportion.When Ce substitution is at 30%,(BH)max can reach 40MGOe.With a same (BH)max, corrosion resistance of Ce-containing and Ce-free magnets exhibits little difference.Controlling micro-structure,such as the atomic position of Ce in magnetic phases can further improve the performance of sintered (Ce,Nd)-Fe-B magnets.

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