Unveiling the enhancement of mechanical properties in cryogenic-treated Sm_2Co_{17} permanent magnets without sacrifice of magnetic properties

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Abstract

SmCo permanent magnets are used in some of the strongest permanent magnets, particularly for applications between about 200 and 550°C. However, their brittleness limits their practical use. Improving their mechanical properties is therefore of great practical significance. Cryogenic treatment is firstly applied in SmCo permanent magnets to enhance the mechanical properties. The flexural strength has been increased by 13.6% along the weakest orientation, and the anisotropy of thermal expansion has been reduced by 18.2%. The magnetic properties are almost the same despite of cryogenic treatment, which is different from other method to improve mechanical properties at the cost of magnetic properties deterioration. The flexural strength enhancement primarily stems from residual stress decreasing, while the anisotropy reduction of thermal expansion is closely related with lattice constants decreasing. This

study provides an effective and convenient approach to enhance the mechanical properties in Sm_2Co_{17} permanent magnets without sacrifice of magnetic properties.

Keywords**:** Sm_2Co_{17} permanent magnets; Cryogenic treatment; Mechanical properties; Thermal expansion anisotropy; Residual stress.

Rare-earth permanent magnets have found widespread applications in various fields, including electric vehicles, wind power generation, and electronic devices[1]. Sm_2Co_{17} permanent magnets boast higher coercivity, superior temperature stability, and excellent corrosion resistance. As a result, Sm_2Co_{17} permanent magnets exhibit distinct advantages in aerospace, military industries, and high-reliability microwave communication applications[2].

The crystal structures of $SmCo_5$ and Sm_2Co_{17} compounds are hexagonal and rhombohedral, respectively, and neither of them possesses a sufficient number of slip systems to accommodate plastic deformation [3]. Consequently, these materials are inherently brittle, relying on intracrystalline cleavage for fracture propagation. It makes them prone to breakage, cracking, or fracturing during magnet manufacturing and assembly processes, resulting in high manufacturing losses (up to 20-30%) despite careful handling[4]. The brittleness limits the shape and size of the magnets, rendering them unsuitable for certain applications [5-7]. It is therefore of great practical significance to improve the mechanical properties.

Previous research has demonstrated that the brittleness of Sm-Co magnets can be mitigated through the design of their microstructure and optimization of processing techniques, such as adjusting grain size distribution and applying surface coatings [8-15]. For example, the flexural strength of Sm-Co magnets can be improved by adjusting the grain size distribution[4, 11]. Coating the surface of Sm-Co magnets with a metal layer enhances their fracture toughness, flexural strength, and tensile strength[12, 13]. The impact toughness of Sm-Co magnets has been improved by adding trace amounts of high melting point ZrB_2 (zirconium boride) particles in the powder-making process[14]. Additionally, the mechanical anisotropy of Sm_2Co_{17} permanent magnets can be mitigated by adjusting the Zr content[15]. However, these improvements in mechanical performance have some adverse effects on magnetic properties, as well as increased cost and complexity in processing, and challenges in product recyclability[16, 17].

In deed, the mechanical properties of the alloy can be improved by a convenient method. Cryogenic treatment has the ability to refine the grain structure of steel, enhancing the effect of grain boundary strengthening and improving both yield strength and tensile strength. Additionally, it can eliminate or reduce defects and stress within the steel, thereby enhancing fracture toughness and impact resistance, ultimately enabling the steel to better withstand external forces and deformation[18-20].However, the effects of cryogenic treatment on the mechanical properties and magnetic properties of Sm_2Co_{17} permanent magnets yet to be explored.

The cryogenic treatment is firstly applied in Sm_2Co_{17} permanent magnets to enhance the mechanical properties in this study. Meanwhile, the effects of cryogenic treatment on magnetic properties have been investigated. The results show that the flexural strength is increased by 13.6% along the weakest orientation, while the anisotropy of thermal expansion is reduced by 18.2% . In addition, cryogenic treatment slightly increased intrinsic coercivity (29.45 kOe to 30.96 kOe), while other magnetic properties remained mostly unchanged. The flexural strength enhancement primarily stems from residual stress decreasing, while the anisotropy reduction of thermal expansion is closely related with lattice constants decreasing. This study provides an effective and convenient approach to enhance the mechanical properties in Sm_2Co_{17} permanent magnets without sacrifice of magnetic properties.

The investigated alloy with a nominal composition of $Sm(Co_{bal}Fe_{0.22}Cu_{0.06}Zr_{0.023})_{7.92}$ was fabricated by induction melting. The dimensions of the sample for flexural strength are as follows: length (l) × width (b) × height (h) = 40 mm × 4 mm × 3 mm. Samples cut from the same magnet are divided into three groups based on their orientation with respect to the easy magnetization c-axis of Sm_2Co_{17} permanent magnets: *l//c*, *b//c*, and *h//c*. The group numbers are listed in Table 1, with each group containing seven samples. The Vickers hardness test samples are cylindrical with a diameter and height (H) of 10 mm. To examine the relationship between height (H) and the c-axis orientation, they are divided into two groups: H parallel to the c-axis ($H//c$) and H perpendicular to the c-axis ($H \perp c$), as also indicated in Table 1. Each group consists of five samples. The magnet types are classified as A and B based on different processing conditions. Magnet A represents untreated samples, while magnet B represents samples subjected to a 30-minute cryogenic treatment.

Table 1. Conditions of treatment Sm_2Co_{17} permanent magnets and the group number of bending and hardness samples.

Magnet type	Group number of bending samples			Group number of hardness samples		Processing condition
	$l//c$	$b//c$	$h//c$	$H // c$	$H \perp c$	
A	A_1	A_2	A_3	A_4	A_5	Untreated
B	B_1	B_2	B_3	B_4	B_5	Cryogenic treatment

Bending tests are conducted using a universal testing machine (Roell Z030, Germany) with a pre-load of 3 MPa and a loading rate of 0.5 mm/min. The flexural strength is determined using a three-point bending test, with a span length (Ls) of 30 mm and loading along the 3 mm height direction. The Vickers hardness measurements are performed using an MH-500D microhardness tester controlled by the EM-5002A software system. The tests are conducted at room temperature, with the maximum load set at 9.8 N and a loading duration of approximately 10-20 seconds. Phase analysis is carried out using a Rigaku SmartLab X-ray powder diffractometer equipped with a Cu Kα radiation source. Microstructural analysis of the prepared samples is conducted using a G300-type scanning electron microscope (SEM) equipped with an energy-dispersive X-ray spectroscopy (EDX) and an automated electron backscatter diffraction (EBSD) analysis system. The OIM software is employed for residual stress analysis. Thermal expansion curves are obtained using a thermal mechanical analyzer (TMA) at a heating rate of 5 K/min, in the temperature range of -120°C to 900°C.

The flexural stress-strain curves before and after cryogenic treatment exhibit similar characteristics, as shown in Figure 1(a) and (b). There is no yield stage before reaching the maximum bending load, indicating a typical brittle fracture behavior. For the three groups of samples (*l//c*, *b//c*, and *h//c*) with and without cryogenic treatment, the flexural strength exhibits anisotropy [8, 9], as shown in Figure 1(c). The samples with *h//c* orientation shows the highest flexural strength, followed by the *b//c* orientation, while the samples with *l//c* orientation has the lowest strength. It is noteworthy that the observed anisotropic pattern in this case deviates slightly from the reported results in the literatures[9, 10]. It could be attributed to the different content of Zr element. Previous studies have found that for magnets with lower Zr content, the flexural strengths of the *h//c* and *b//c* groups are comparable and significantly higher than that of the *l//c* group [15]. It is consistent with the observed pattern of flexural strength in our experimental magnets. It is worth noting that the *l//c*, *b//c*, and *h//c* groups, the flexural strength after cryogenic treatment is increased by 13.6%, 6.3%, and 2.6%, respectively. It indicates that flexural strength of Sm_2Co_{17} permanent magnets can be enhanced by cryogenic treatment.

As shown in Figure 1(d), there is also an anisotropic behavior in Vickers hardness with and without cryogenic treatment. Overall, the Vickers hardness is greater for samples with height perpendicular to the easy magnetization c-axis ($H \perp c$) compared to those with height parallel to the c-axis ($H \parallel c$). Furthermore, a decrease in Vickers hardness is observed after cryogenic treatment. Specifically, the Vickers hardness of samples with height perpendicular to the c-axis ($H \perp c$) decreases by 3.8%, while the hardness of samples with height parallel to the c-axis ($H \parallel c$) decreases by 1.7%. In summary, cryogenic treatment significantly improves the flexural strength of Sm_2Co_{17} permanent magnets. Additionally, vickers hardness is slightly decreased by cryogenic treatment.

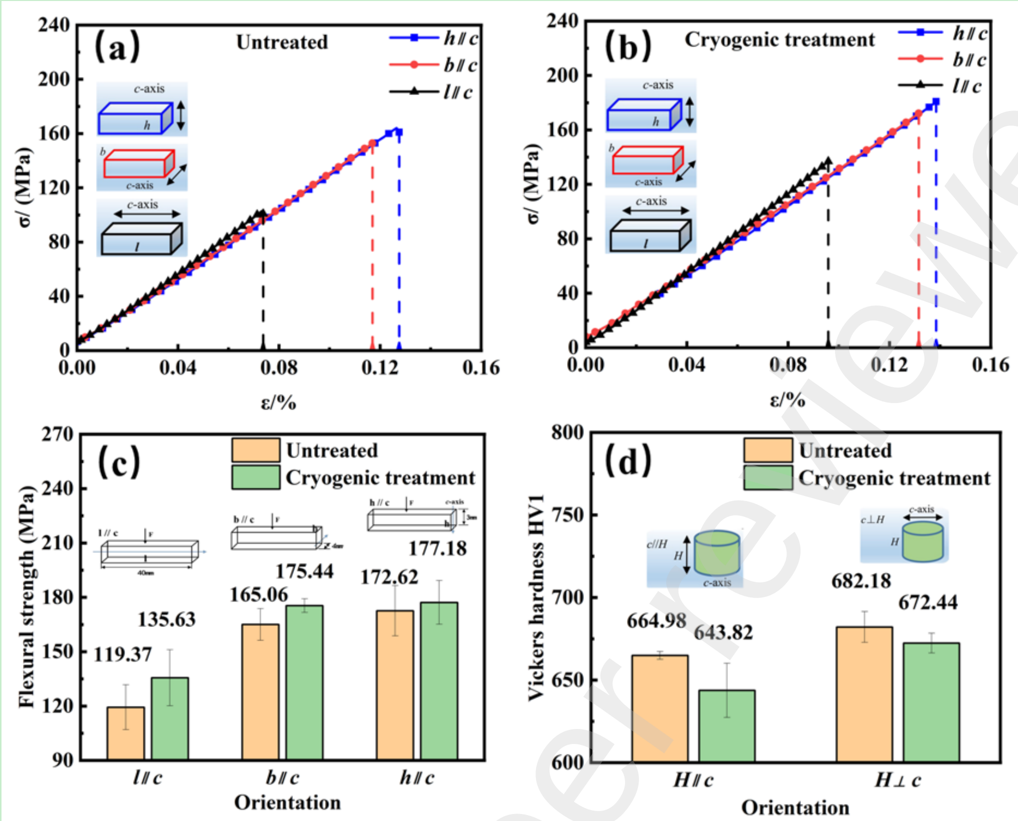


Figure 1:(a) and (b): Stress-strain curves with and without cryogenic treatment; (c) Changes in flexural strength with and without cryogenic treatment; (d) Changes in Vickers hardness with and without cryogenic treatment.

The changes in thermal expansion with and without cryogenic treatment are depicted in Figure 2(a). It can be observed that both the untreated and cryogenically treated samples do not exhibit significant linear variations in thermal expansion. Besides, they demonstrate anisotropic behavior along the *//c* and $\perp c$ directions. The thermal expansion rate is higher in the $\perp c$ direction, indicating greater lattice point vibrations in the crystal lattice along that orientation with temperature changes. As the temperature increases, the anisotropy initially increases and then decreases. At approximately 780°C, the maximum disparity in anisotropy is observed. As the temperature surpasses 780°C, the anisotropy diminishes. This phenomenon is attributed to the gradual transition of Sm_2Co_{17} magnets from ferromagnetic to paramagnetic behavior at around 780°C, resulting in a reduction in magnetic crystal anisotropy [21, 22]. As shown in Figure 2(a), the average linear expansion coefficients for the untreated sample in the $\perp C$ and $//C$ orientations are 13.997 × 10^{-6}/K and 9.862 × 10^{-6}/K, respectively. By calculating the difference in average linear expansion coefficients (Δa) between the $\perp C$ and $//C$ orientations of the untreated magnet, the anisotropic thermal expansion difference of the magnet untreated is 4.135×10^{-6} / K.

Similarly, the average linear expansion coefficients for the cryogenically treated sample in the $\perp C$ and $//C$ orientations are 13.523 × 10^{-6}/K and 10.139 × 10^{-6}/K, respectively. By calculating the difference in average linear expansion coefficients (Δa) between the $\perp C$ and $//C$ orientations of the cryogenically treated magnet, the anisotropic thermal expansion difference of the magnet after cryogenic treatment is 3.384×10^{-6} / K. Comparing these two values, it can be observed that the anisotropy decreases after cryogenic treatment. The cryogenically treated sample exhibits a reduction of 18.2% in anisotropy of thermal expansion compared to the untreated sample. Therefore, cryogenic treatment can effectively reduce the thermal expansion anisotropy of the Sm_2Co_{17} permanent magnets.

The magnetic performance curve of the same magnet, before and after cryogenic treatment, is depicted in Figure 2(b).Cryogenic treatment slightly increased intrinsic coercivity (29.45 kOe to 30.96 kOe), while other magnetic properties remained mostly unchanged. This demonstrates that cryogenic treatment without sacrifice of magnetic properties.

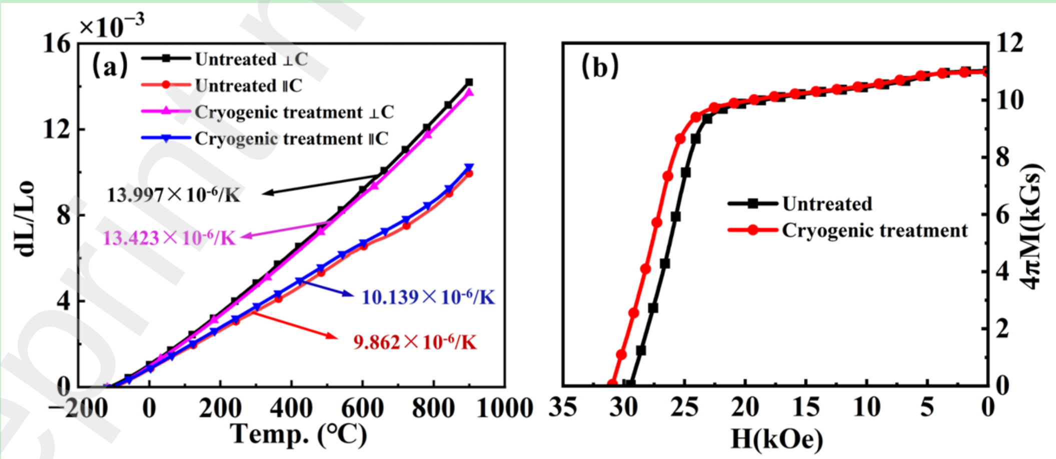


Figure 2 (a) the thermal expansion curves with and without cryogenic treatment (according to the relationship between the test head and the easy magnetization axis (C axis), divided into two orientations: $//C$ axis and $\perp C$ axis). (b) the magnetic property curve before and after cryogenic treatment

In order to unveil the reasons for the improvement in mechanical performance and the reduced anisotropy of thermal expansion were investigated through XRD phase analysis, as illustrated in Figure 3(a) and (b). The results show that the diffraction peak positions are relatively consistent, and no new peaks are observed. It indicates that the phase composition remains unchanged with and without cryogenic treatment, consisting of the 2:17R and 1:5H phases. Moreover, the XRD powder data are further refined using the Rietveld method and FullProf software. It is worth noting that the lattice constants of the untreated magnet are a = 0.848887nm and c = 1.23074nm, while the lattice constants of the cryogenically treated magnet are a = 0.848163nm and c = 1.227935nm. These results indicate that cryogenic treatment leads to a small decrease in lattice constants and a reduction in lattice spacing. Decreased lattice constants strengthens the gravitational forces between atoms, enhancing the resistance against expansion caused by thermal vibrations and reducing the anisotropy of thermal expansion. In addition, in-situ EDX analysis was conducted to analyse the composition change as shown in Figure 3(c) and (d). It can be observed that the distribution of the major elements does not exhibit significant changes.

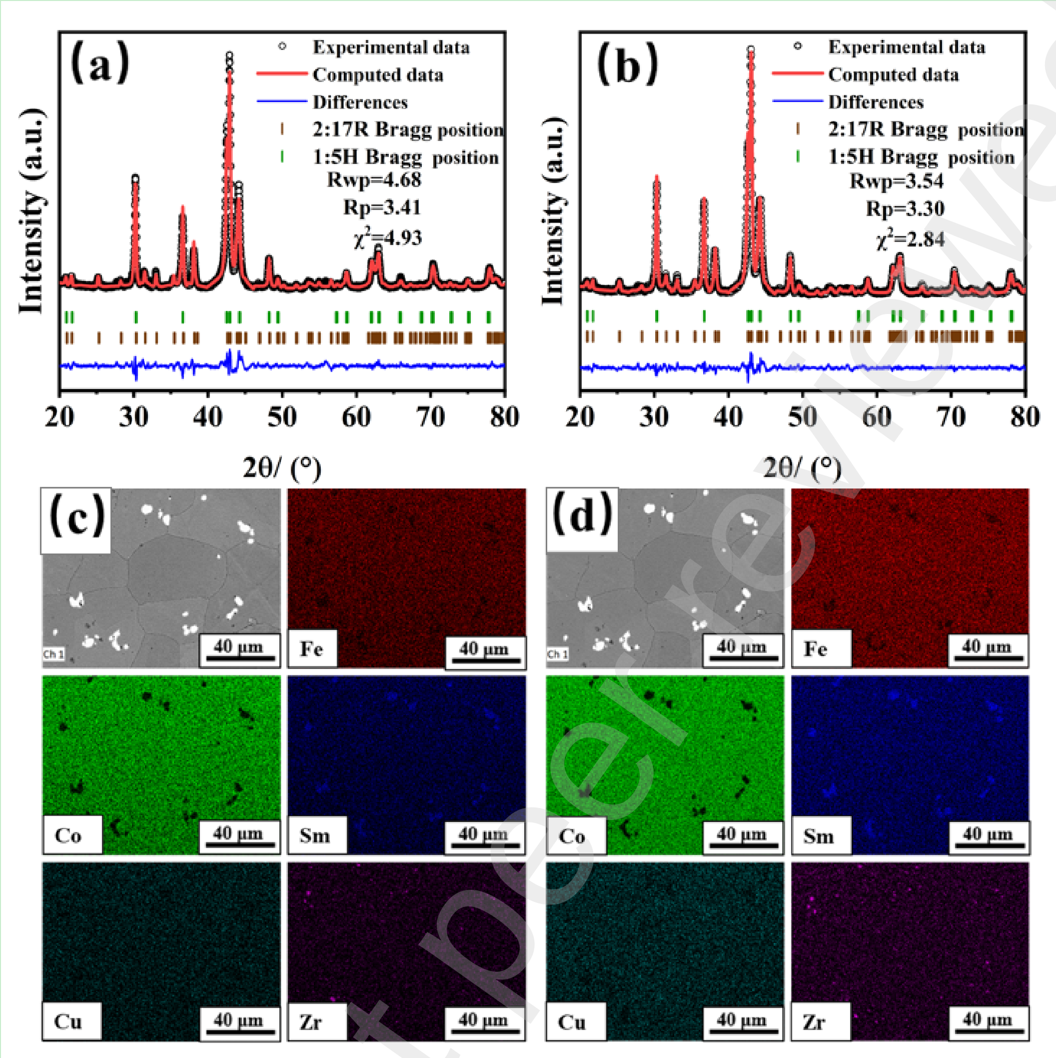


Figure 3 (a) and (b) show XRD refinement results before and after cryogenic treatment, (c) and (d) represent before and after in-situ scanning after cryogenic treatment.

In order to analyze the reasons behind the improvement in flexural strength, further investigation was conducted through quasi in-situ EBSD analysis to examine the variations in residual stresses. Figures 4(a, c), and (e, g) present the distribution maps of Kernel Average Misorientation (KAM) before and after cryogenic treatment. These visualizations reveal the disparities in orientation between the untreated magnet and the one subjected to deep cryogenic treatment, primarily concentrated within the range of 0° to 3°. Further analysis the KAM_{ave} value decreased from 0.670 to 0.634 for the perpendicular orientation to the C-axis, while for the parallel orientation, it decreased from 0.737 to 0.680. This observation indicates that the KAM_{ave} of the magnet decreases after cryogenic treatment.

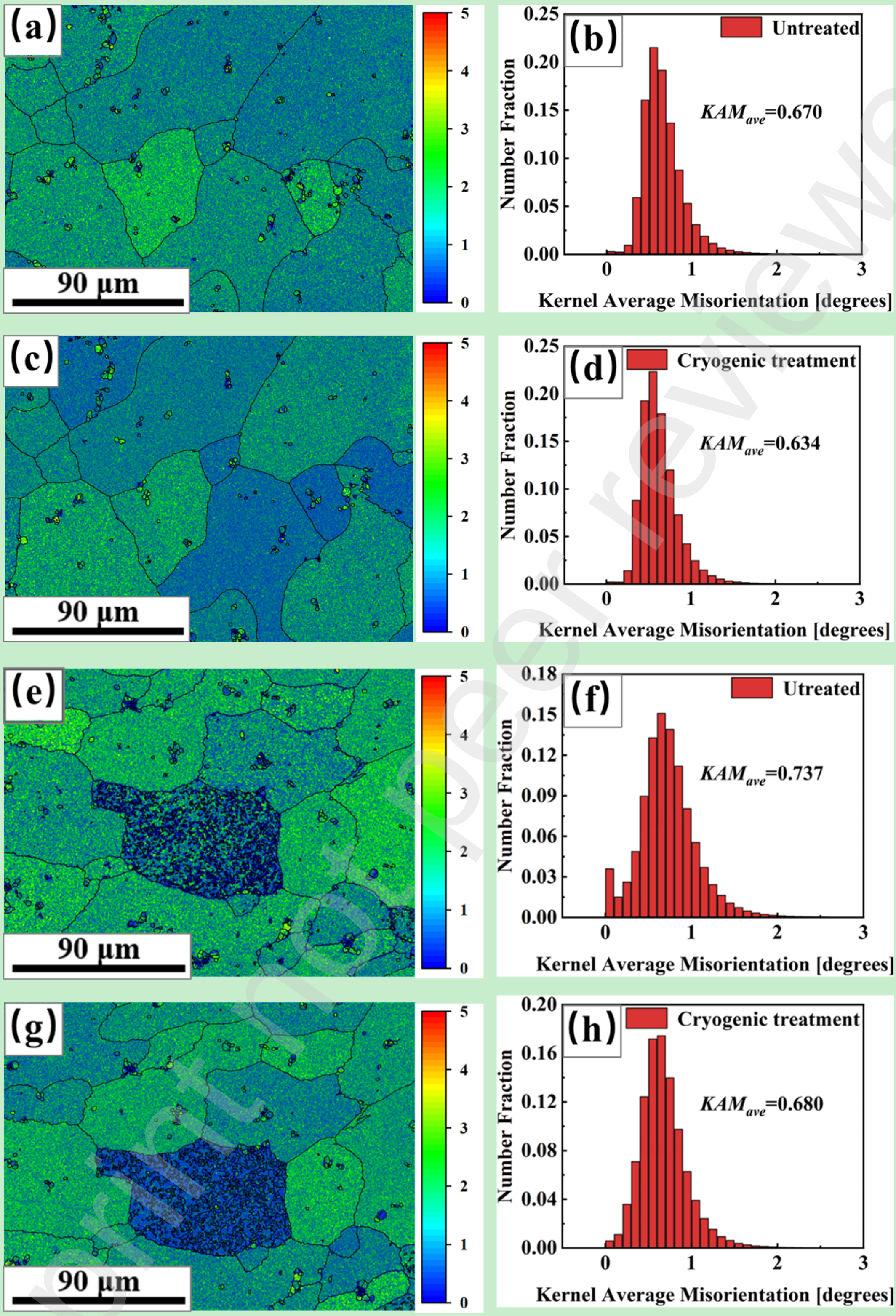
As an index to analyze geometric dislocation densities (GND) during plastic deformation, KAM is a core point composed of 24 nearest adjacent points, and each point is assigned a scalar value to represent its local misorientation [23, 24]. The KAM_{ave} value can be calculated by Eq. (1)

$$\Delta\theta_i = \frac{1}{n}\sum_{j=1}^{n} |\theta_{j^{sur}} - \theta_i| \quad (1)$$

Where $\Delta\theta_i$ represents the local misorientation at point i, θ_j^{sur} is the misorientation at its adjacent point j, and n represents the number of points in the test region. An approximation of GND densities can be obtained from KAM_{ave} values. According to strain gradient theory[25], Eq. (2) can be used to extrapolate the GND density.

$$\rho^{GND} = \frac{2\Delta\theta_i}{\mu b} \quad (2)$$

where $\Delta\theta_i$, μ, and b are the KAM_{ave} value, the EBSD step size for data acquisition, and the magnitude of the Burgers vector, respectively. The μ and b in this context are constant, therefore, the GND density value is solely dependent on the value of KAM_{ave}. These findings indicate that cryogenic treatment has a positive effect on the GND density of the material, reducing the dislocation density. Reducing the GND density typically leads to a decrease in residual stresses within the material, suggesting that deep cryogenic treatment can reduce residual stresses in the material.



Figures 4(a,c), (b,d) show KAM distribution and average values for samples perpendicular to C-axis before and after cryogenic treatment. Figures 5(e,g) , (f,h) depict the same for samples parallel to C-axis.

During the heating and cooling process, the difference in temperature change rates between the centre and outer surface of the sample can result in the generation of internal stresses. Figure 5(a) depicts a schematic of the cooling behavior of the magnet after the secondary aging. From time t_0 to t_1, the surface cools more rapidly compared with the centre. Due to the inhibiting effect of the centre on the surface (the centre pulls the surface layer, hindering its contraction), the surface experiences tensile stress while the centre experiences compressive stress. The recovery process of the cryogenically treated magnet from -196°C to room temperature is depicted in Figure 5(b). From time t_2 to t_3, the surface warms up more rapidly compared with the centre. Similarly, due to the inhibiting effect of the centre on the surface (the centre puts pressure on the surface layer, hindering its expansion), the surface experiences compressive stress while the centre experiences tensile stress. By comparing the processes from time t_0 to t_1 and from time t_2 to t_3, it can be concluded that cryogenic treatment helps to neutralize the residual stresses generated during the heat treatment process. Extensive researches have shown that residual stresses have an impact on the mechanical performance of different engineering systems. This is because when residual stresses are present in a structure, a portion of the strength is used to overcome stress trapped within it, resulting in premature catastrophic failure [26-28]. Cryogenic treatment can effectively reduce residual stress within the Sm_2Co_{17} permanent magnets,which is crucial for enhancing the mechanical properties and durability.

In addition, the production of sintered Sm_2Co_{17} permanent magnets often faces the issue of cracking, which falls within the realm of mechanical performance. Tian Jianjun [21, 22] and others have investigated the quench cracking problem in radially oriented sintered rings of Sm_2Co_{17} permanent magnets, pointing out that the significant thermal expansion anisotropy during the quenching process is the primary cause of cracking in the ring magnets. Cryogenic treatment, by reducing lattice constants and optimizing crystal arrangement, mitigates the thermal expansion anisotropy of the material, improves the expansion uniformity at high temperatures, thus reducing the occurrence of cracking issues.

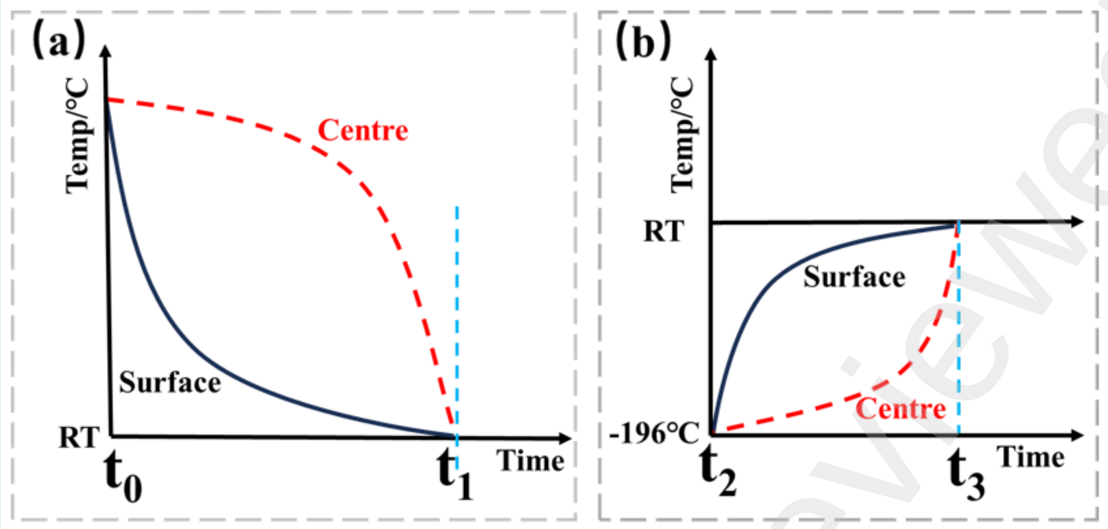


Figure 5: (a) the depicts a schematic of the cooling behavior of the magnet after the secondary aging, and (b) the schematic diagram of the magnet recovering from -196℃ to room temperature after cryogenic treatment.

In this study, we have employed cryogenic treatment as a pioneering approach to augment the mechanical properties of Sm_2Co_{17} permanent magnets. Meanwhile, the effects of cryogenic treatment on magnetic properties have been investigated. Notably, cryogenic treatment slightly increased intrinsic coercivity (29.45 kOe to 30.96 kOe), while other magnetic properties remained mostly unchanged. The flexural strength has experienced a remarkable surge of 13.6% along the weakest orientation, with this enhancement predominantly arising from the mitigation of residual stress. Furthermore, the anisotropy of thermal expansion has been significantly reduced by 18.2%, and this decrease aligns closely with the diminishing lattice constants. This study provides an effective and convenient approach to enhance the mechanical properties in Sm_2Co_{17} permanent magnets without sacrifice of magnetic properties.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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