Sparkling Plasma Sintering Method for Developing Cube Textured Ni7W/Ni12W/Ni7W Multi-Layer Substrates Used for Coated Conductors

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Abstract: Mechanically strengthened, highly cube textured Ni-7at.%W/Ni-12at.%W multi-layer substrates used for coated conductors have been prepared by advanced spark plasma sintering technique. The key innovation for developing this weakly magnetic and reinforced substrate was to use a new powder metallurgy and sintering route to bond multi-layers of Ni7W-Ni12W-Ni7W together in order to get an initial ingot, then followed by optimized cold working and annealing. Particular efforts were made in view of the optimization of the design, pressing as well as the heat treatment processes of the starting ingots in order to obtain a chemically gradient composite bulk, thus ensuring the subsequent cold deformation of the bulk. The produced composite substrates have a strong <001> \ {100} texture on the top Ni7W outer layer determined by EBSD and X-ray. The percentage of the biaxially orientated grains within a misorientation angle of 10° is as high as 97.5%, while the length percentage of low angle GBs ranging from 2° to 10° in the composite substrate reaches 87.2%. Moreover, the yield strength \( \sigma_{0.2} \) of the tape approaches 333 MPa, and the saturation magnetization is substantially reduced by 81.6% at 77K when compared to that of a commercial used Ni5W substrate.
1. Introduction

Pure Nickel and its alloy tapes with sharp cube texture have been demonstrated in Oak Ridge National Laboratory (ORNL) through Rolling Assisted Biaxially Textured Substrates (RABiTSTM) route in last decade [1-3]. Until now, hundreds lengths of textured Ni-5at.%W (Ni5W) substrates have been successfully prepared and engaged in the production of coated conductors [4,5]. However, the question for how to improve the mechanical and magnetic properties of Ni5W alloy tapes was still remaining and becoming one of the obstacles for developing some practical applications of the coated conductors. In order to solve these problems, several ideas were put forward as followings: One is to increase the content of Tungsten in NiW alloy, such as Ni-7at.%W or Ni-9at.%W. Unfortunately, the sharp cube texture could not be easily formed in these high Tungsten Ni alloys due to their low Stack Fault Energy (SEF) [6]; Another alternative is to fabricate a composite tape with sandwich-like structure using a sharp cube textured Ni5W outer layer on a hard Ni alloy core in order to increase the mechanical strength while decreasing the magnetization of the whole substrate. Researchers both in IFW Dresden and Superconducting Research Laboratory (SRL) in Japan have made many efforts to prepare such composite substrates using the TIT (Tube in Tube) or the PIT (Powder in Tube) processes [7, 8]. However, these methods produce only a mechanical bond between outer and inner layers, which inevitably leads to a separation of tri-layers during deformation, even when a hot rolling step was employed. In our recent works, several kinds of Ni5W/Ni12W/Ni5W tapes were successfully fabricated by the novel “Layer by Layer” routes using either traditional Cold Isostatically Press (CIP) or Advanced Sparking Plasma Sintering (SPS) techniques [9, 10]. Using these methods, a gradient ingot was sintered to ensure the subsequent cold deformation of the starting material without any hot rolling process.

In order to further improve both the mechanical strength and the magnetization of the substrate, in this work, a new Ni-7at.%W/Ni-12at.%W/Ni-7at.%W tri-layer substrate has been prepared. Due to the strength joint between the outer and inner layers of the composite tapes, the delamination of the layers was not observed during heavy cold rolling processes even though there exists a large difference of the mechanical hardness between outer and inner layers. The micro-orientation, misorientation angle and the grain alignment on the Ni7W surface layer of the as fabricated composite substrate were analyzed by X-ray and EBSD. The improvement of the yield strength and magnetic properties of the composite substrate was discussed.

2. Experimental

Advanced Sparking Plasma Sintering technique was used to prepare the Ni-7at.%W/Ni-12at.%W/Ni-7at.%W starting composite ingots. The details of the processes for fabricating such NiW alloy composite tapes were very similar as what we have reported in our previous work [9, 10]. Firstly, three pieces of precursor alloy ingots were respectively synthesized by SPS technique [11]. Then, they were put into a graphite die according to the sequence of Ni7W ingot-Ni12W ingot-Ni7W ingot, followed by sintering to joint them together by SPS (3.20MK-V) at 900°C for 5 min. The sintered composite ingot was post-annealed at 1300°C in a flowing Ar (4%H2) gas for 10 hours, followed by cold rolling to 100μm of thickness, the total reduction being larger than 98%. As-rolled composite metallic
tapes were heat treated through an optimized two-step annealing process [12] by holding the sample at a lower temperature (about 750°C) for half an hour before reaching the annealing temperature of 1350°C in a flowing Ar (4%H2) atmosphere in order to get the required orientation at the top surface of the composite substrate.

The recrystallisation texture and the GBs characterization of the composite tapes were detected by electron backscattering diffraction (TSL, equipped in JEOL JSM 6500) on an area of 400×600 μm². Furthermore, the (111) phi scan and the rocking curve of the tapes were measured by X-Ray four circle diffractometer (SIEMENS D5000) using Cu Kα radiation. The stress curves were determined by a SCHENCK TREBEL RSA250 tensile machine (with ) on tapes of 75 mm length and 10 mm width, under a speed of 3 mm/min. A Quantum Design (PPMS9) magnetometer was used to measure the M-H hysteresis loops at 77 K in order to examine the magnetization of the as fabricated composite tapes.

3. Results and Discussion

The micro-texture of the outer layer in the composite substrates was characterized by EBSD, and the date was collected from a hexagonal grid at a spacing of 4 μm in a substrate region of 400×600 μm². All the data was processed and analyzed by Orientation Image Micrograph (OIM-TSL, version 5.2). As shown in Fig. 1, the percentage of the cubic orientation on the thin top Ni7W layer of the composite substrate within a misorientation angle of 10° was reached as high as 97.5%, while the percentage of the grain alignments (shown in Fig.2) within (001) <100> orientation nearly approached 100% when the specified alignment angle is 12°, which has performed sharper cube texture than that of a single Ni7W substrate prepared by the same route. This was possibly resulted from the different deformation and recrystallization mechanism between the multi-layer and mono layer tapes. The fully understanding of the forming mechanism of the cube texture in the Ni7W layer of the composite substrate is still under studying.

![Figure 1. EBSD mapping of the top layer in the composite substrate measured on a region of 400×600 μm².](image1)

In the figure 3, the full width of half maximum (FWHM) values of 7.08° and 5.48° were calculated by Gaussiann fit from the X-ray (111) Phi scans and the (200) rocking curves.

![Figure 2. The distribution of the grain alignments within (001) <100> orientation](image2)
data (along the rolling direction), respectively, indicating both sharp a-b axial and c-axial orientations of the tape surface in our composite substrates. These results illustrate that a high quality of texture performance on outer layer of the composite substrate has been obtained.

![Figure 3](image)

**Figure 3.** a) (111) phi-scan and b) (200) rocking curve in the out layer of the composite substrate.

The length percentage of Low-angle GBs on the tape surface is another essential characterization for textured substrates. The *Number Fraction Vs. Misorientation Angle* curve was plotted in figure 4. For statistic, any point pair with misorientation angle exceeding 2° is regarded as a grain boundary. It is observed that there are large amounts of low-angle GBs on the selected area of the tape surface of the composite substrate. By calculation, the length fraction of the GBs between the misorientation angles ranging from 2° to 10° reaches 87.2%.

![Figure 4](image)

**Figure 4.** GBs misorientation angle characterization: the distribution of Number fraction vs. Alignment

As the content of Tungsten has serious effect on the magnetic and mechanical properties of Ni-W alloy substrates, so that the configuration of the composite substrate by using Ni12W as a core layer and Ni7W as outer layers was expected to reduce the ferromagnetism and increase the overall mechanical strength of the textured composite tapes. The Stress-Strain curves of the several kinds of annealed tapes (Ni5W, Ni7W and as-obtained composite tapes)
measured under axial tension at the room temperature were then plotted together in Fig.5. The loading direction was along the [001] crystallographic direction of the textured substrates during the measurements. It can be seen that the composite tape exhibits high yield strength: the value of $\sigma_{0.2}$ is 333 MPa, dramatically exceeding that of Ni5W and Ni7W tapes by a factor of more than 2 and 1.5, respectively.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig5.png}
\caption{The tensile stress-strain curves of the Ni5W, Ni7W and the Ni7W/Ni12W/Ni7W composite tapes measured at room temperature.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig6.png}
\caption{Magnetization loop at 77 K for the Ni7W/Ni12W/Ni7W composite substrate (The inset shows the M-T curve of the tape under 1000 Oe).}
\end{figure}

In the practical application of the coated conductors, the lower the saturation magnetization of the tapes, the less energy loss will be generated in AC current transmission processes [13]. Figure 6 shows the M-H hysteresis loops at 77 K for the annealed composite substrates. It is found that the hysteresis losses are dramatically decreased in the substrate, and its saturation magnetization at 77K is 5.04 emu/g, which is reduced significantly by 81.6% at 77 K when compared to that of Ni5W substrates (27.4 emu/g) [13]. The inset shows that the nominal Curie temperature of the composite tape is as low as 188 K. The reduction of both the saturation magnetization and Curie temperature is attributed to the utilization of both Ni12W and Ni7W materials in the composite tape. Furthermore, deposition of high quality of epitaxial La$_2$Zr$_2$O$_7$ MOD buffer layer directly on this composite substrate proves that the as developed composite substrate is appropriate for the further development of the coated conductors, which will be presented separately.

4. Conclusions

In conclusion, we have developed a new composite material to be used as a substrate in coated superconducting tapes. The sandwich-like composite substrates was designed and prepared by configuring Ni7W alloy as outer layers and Ni12W alloy as a core layer of a composite material, followed by sintering through SPS technique and optimized cold working as well as the recrystallization processes. It was found that the surface of Ni7W outer layer in this composite tape presents a sharp $\{100\} <001>$ cube texture. Moreover, the yield strength ($\sigma_{0.2}$) of the composite tape reaches 333 MPa, exceeding that of the commercial used Ni5W substrates by a factor of 2, while the saturation magnetization of this composite substrate is 5.04 emu/g at 77 K. Consequently, it is strongly believed that the development of the highly
reinforced and biaxially textured composite substrate by this innovated approach could be a very promising alternative to the commercial used Ni5W alloy substrate in the near future.

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