Time-of-Flight Neutron Small-Angle Scattering from a Superconducting Composite Wire

BY KOZO OSAMURA, HIROSHI TSUNEKAWA AND YOTARO MURAKAMI
Department of Metallurgy, Kyoto University, Sakyo-ku, 606 Kyoto, Japan

MASAYOSHI ONO, HIROYUKI YOSHIDA AND SUNAO OKAMOTO
Research Reactor Institute, Kyoto University, Kumatori, 590-04 Osaka, Japan

AND YOSHIYUKI MONJU AND TOSHIRO FUKUZUKA
Asada Research Laboratory, Kobe Steel Ltd, Nada-ku, 657 Kobe, Japan

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Abstract
The precipitation behavior in the Ti–27at.%Nb–6at.%Ta–6at.%Zr alloy aged at 643 K was examined by means of time-of-flight neutron small-angle scattering. When the alloy was aged, fine-scale \( \alpha \) precipitates appeared. During the precipitation process, each precipitate grew in size, but the total number of precipitates remained nearly constant up to 1 Ms of ageing. The increase of critical superconducting current density could be connected with increasing size of \( \alpha \) precipitates. The specimen for the measurements consisted of a composite containing 3721 filaments in a copper matrix. The use of neutrons was shown to give great advantages for the investigation of precipitation phenomena.

1. Introduction
Commercial superconducting composite wires consist of a bundle of thin Nb-based alloy filaments in copper, heavily cold-drawn up to 99.999% reduction in area and given an ageing treatment. It has been found that the final ageing treatment greatly improves the superconducting properties and this is attributed to the fine-scale precipitation of the \( \alpha \) phase (Osamura, Matsubara, Miyatani, Murakami, Horiuchi & Monju, 1980). Metallographic investigation is important for an understanding of the interaction of magnetic flux with the microstructure, but also for the development of higher-performance products. However, the filaments are so heavily drawn and so thin that the structural investigation is difficult. One of the useful techniques is small-angle X-ray scattering (SAXS) as demonstrated previously (Osamura et al., 1980). Size, volume fraction and interparticle separation of the precipitated \( \alpha \) phase were determined in some commercial wires.

The use of neutrons instead of X-rays in small-angle scattering measurements has great advantages for the present purpose. Owing to the large transparency of the sample to neutrons, it is possible to study large samples non-destructively. As titanium has a negative scattering length, but other elements have positive lengths, a large SAS intensity is expected. The present report shows the usefulness of neutron measurements through the description of the experimental results for a commercial superconducting composite wire.

2. Experimental method
The specimen for small-angle neutron scattering (SANS) measurements was a rod with a diameter of 0.74 cm as shown in Fig. 1, in which 3721 super-

Fig. 1. Cross section of the superconducting composite with a diameter of 0.74 cm used for SANS measurements, showing Ti–alloy filaments embedded in a copper matrix.
conducting filaments with an average diameter of 60 μm were embedded in a copper matrix. The alloy composition was Ti-27at.%Nb-6at.%Ta-6at.%Zr. In the as-drawn state, the reduction in area was 99.993%.

To examine the precipitation behavior, the specimen was aged at 643 K for various periods.

SANS measurements were performed by means of the time-of-flight (TOF) technique, using polychromatic pulsed neutrons from a chopper installed at Kyoto University Research Reactor (Ono, 1981a, b). The experimental arrangement is schematically shown in Fig. 2. The polychromatic pulsed neutrons from 0.05 to 0.6 nm were produced by the chopper rotor B whose slit form is parabolic with a curvature coinciding with the trajectory of a neutron with the wavelength of 0.48 nm at the characteristic rotational speed of 40 r s⁻¹. The flight path lengths from the chopper to the sample and from the sample to the detector were 3 m. Two BF₃ counters F were installed at scattering angles of ±0.75° after fine collimator E. The dimension of the incident beam was 0.5 (width) × 4 cm (length) at the sample position. Consequently, the spectrometer may be used in the region of scattering vector \( S \) from 0.1 to 0.7 nm⁻¹, where \( S = 4π \sin θ / λ \).

The wavelength resolution \( Δλ/λ = Δt/t \) was 8.1% at \( λ = 0.1 \) nm, where \( Δt \) is the time resolution determined by the time width of neutron burst and the channel width of the time analyzer, and \( t \) is the time for neutrons to travel the total flight path length. The angular resolution \( Δθ/θ \) was 25% at the end of the fine collimator E.

### 3. Experimental results and discussion

The observed count rates as a function of channel number are shown in Fig. 3. The count rates appearing below about 50 channels are due to parasitic bursts. The channel numbers were transformed to scattering vectors by the relationship \( S = 63.5/(\text{channel No.}) \) (nm⁻¹). As shown in the figure, the spectrum of incident neutrons has a maximum at \( λ = 0.15 \) nm. The count rate for a pure copper rod of the same dimension as the sample was nearly constant over the whole channel range and did not differ much from that measured without any specimen in the sample holder, while the count rates for the specimens aged at 643 K increased as a function of ageing time. The dense arrangement of fine filaments did not give any measurable additional count rate as can be seen from the count rate for the as-drawn specimen, which is nearly equal to that of the pure copper rod. To obtain net values of the scattering intensity from the superconducting filaments, the observed count rates were normalized to the energy spectrum of the incident beam after subtracting the count rates of the pure copper rod.

Fig. 4 shows the corrected scattering intensity vs scattering vector for the specimen aged for various periods at 643 K. The scattering intensity became discernibly larger than the unaged specimen after 18 ks of ageing and successively increased with ageing time. In the higher scattering-vector region, the intensity was proportional to \( S^{-4} \), indicating that Porod's law is
followed in the point collimation condition. The advantage of the TOF technique is that the scattered intensity at low $S$ is not superimposed on the direct beam, a difficulty in experiments using monochromatic neutrons.

Two structural parameters, the Guinier radius $R_G$, which is a sort of radius of gyration, and the integrated intensity $Q$, were obtained from these scattering intensities, as shown in Fig. 5. The integrated intensity was calculated, assuming Porod's law, by the equation
\[ Q = \int_{S_{\text{min}}}^{S_{\text{max}}} 4\pi S^2 I(S) \, dS + 4\pi S_{\text{max}}^3 I(S_{\text{max}}), \]
where $I(S)$ is the scattering intensity and $S_{\text{min}}$ and $S_{\text{max}}$ were adopted as 0.1 and 0.6 nm$^{-1}$, respectively. When the integrated intensity is extrapolated to zero, the corresponding ageing time is seen to be about 10 ks. After this period, both the Guinier radius and the integrated intensity increased remarkably with ageing time. As the present ageing behavior is in good agreement with the previous results obtained by SAXS measurements (Osamura et al., 1980), the scattering intensities observed here are caused by fine precipitates of $\alpha$ phase. The quantity $Q/R_G^3$ gives a relative measure of the number of $\alpha$ precipitates, because the integrated intensity is proportional both to the number and to the volume of precipitates. As seen in Fig. 5, the number of precipitates decreased slightly during the growth of the $\alpha$ phase. The precipitation process of the $\alpha$ phase can be thus described as follows. At the detectable onset of growth beyond 10 ks, the number of these nuclei does not show any further increase. Subsequently each precipitate increases in size, but the total number remains constant at least till 1 Ms of ageing at 643 K.

The correlation between the microstructure and superconducting properties will be now briefly discussed. As is very often found (Osamura, Tsunekawa, Monju & Horiuchi, 1982), the superconducting critical current density at intermediate magnetic fields for this alloy increased during ageing as shown typically in Fig. 6, where the specimen used for the critical current density measurement had the same alloy composition as for SANS measurements, but a slightly different cold reduction rate of 99.998%. The critical current density was very small at the as-drawn state, and increased corresponding to the precipitation of the $\alpha$ phase. During ageing, the number of precipitates did not change considerably, but the size increased by about a factor of two in the ageing period above 18 ks. Although the recovery of the dislocation structure during ageing may be of some importance, it is suggested from the present limited information that the increase of the pinning force is due to the growth of $\alpha$ precipitates.

**4. Summary**

Neutron small-angle scattering measurements were performed non-destructively using a commercial multifilamentary composite of Ti–Nb–Ta–Zr alloy embedded in copper. It was observed that the scattering intensity increases with ageing time at 643 K, and this is attributed to the precipitation of the $\alpha$ phase in the alloy. The present method using neutrons has been proved to be useful for studying precipitation phenomena in superconducting composite wires.

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