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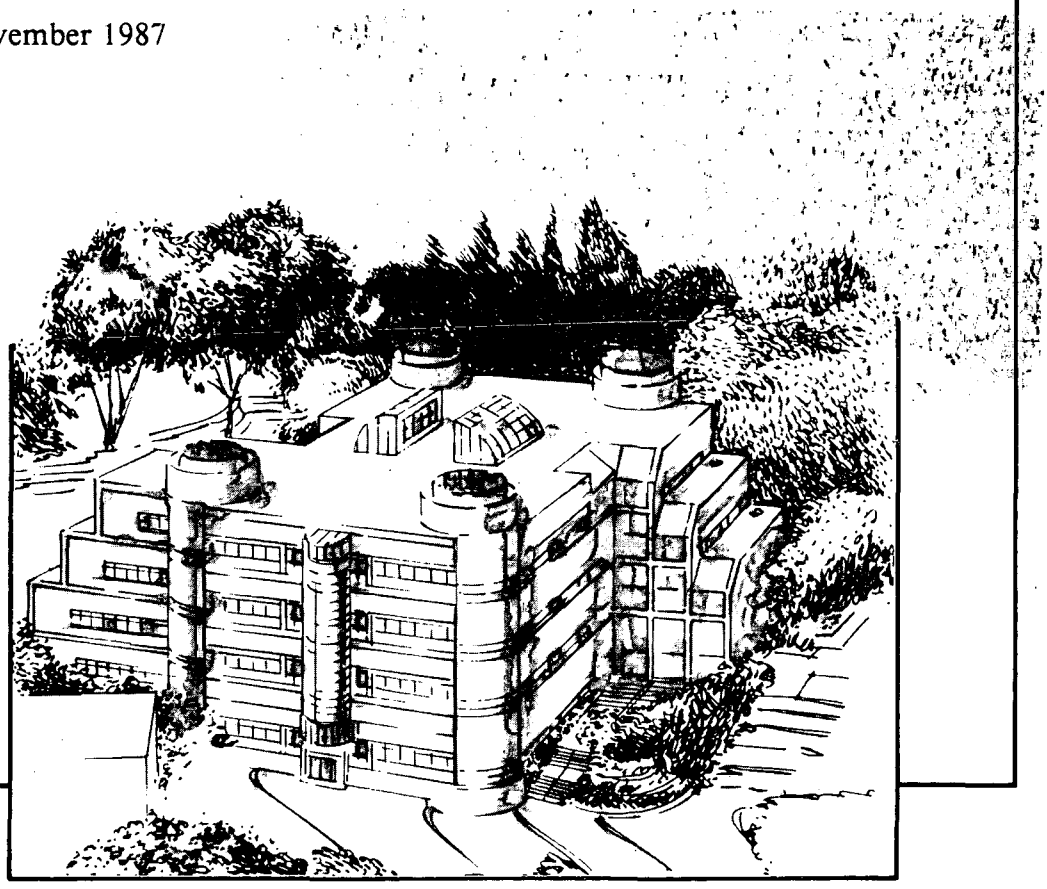

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The critical current density of powder metallurgy processed wires is determined in part by the extent of the A15 phase formation in the vicinity of the Nb/Al interface. A series of multi-layered samples was made to simulate the reactions in the P/M wires. Transmission electron microscopy was used to study the reactions between the multi-layers. The results indicate that the reactions at the Nb/Al interface depend strongly on the Nb and Al layer thickness and distribution. No evidence of the metastable NbAl solid solution formation was found. It is concluded that the Nb_2Al and the residual Nb present in the reacted P/M wires can be avoided if the Nb and Al layers are sufficiently thin and uniformly distributed with the proper stoichiometry.

INTRODUCTION

The critical current density (J_c) of Nb-Al superconducting wires made by the powder metallurgy(P/M) process is determined by the volume fraction, grain size and stoichiometry of the superconducting A15(Nb_3Al) phase. The Nb-Al binary phase diagram[1] indicates that the reacted A15 phase has better stoichiometry at higher reaction temperatures. However grain growth becomes severe at high temperatures, which lowers J_c. Heat treatment temperature ranges between 900~1100°C are commonly used in order to compromise between these effects.[2]~[5] These heat treatments, however, do not change the average A15 grain size and shape substantially. As a result, our study has focused on the factors which determine the A15 (Nb_3Al) phase volume fraction.

It is believed that the A15(Nb_3Al) forms only in the vicinity of the Nb/Al interface. Therefore Nb-Al superconducting wires are made with extremely high reductions in area during wire drawing in order to increase the amount of Nb/Al interface and thus the amount of A15 phase. However the kinetics of the reactions at the Nb/Al interface are not well understood.

We have suggested that the reactions depend strongly on the morphology of the Nb and Al filaments (or layers) before reaction.[6] Since the reactions are limited by the diffusion of Nb and Al, the Nb/Al layers must not only be very thin but also uniformly distributed in order to maximize A15 formation. Sigma phase (Nb_2Al) and residual Nb are found in powder metallurgy processed wires of even extremely high reduction ratios. We postulated that these undesired phases result from uneven distribution of Al and Nb in the powder metallurgy processed Nb/Al wires, caused by the local agglomeration of the powder particles.

Nb_3Al thin films have been widely used to study A15(Nb_3Al) formation.[7]~[10] These thin films are made by co-sputtering, laser beam irradiation or arc melting in order to form a NbAl solid solution. However, the formation of A15 phase from the NbAl solid solution do not represent the reactions at the Nb/Al interface as it occurs in the powder metallurgy processed wires. A15 phase formation has also been characterized in the powder metallurgy processed wire samples.[6],[11] Since the Nb and Al layers in these wires are not homogeneously distributed, it is difficult to obtain valuable information about the effect of the Nb/Al layer configurations on A15 phase formation.

Recently, Bormann et al.[12] studied the reactions between Nb and Al layers using Nb/Al multi-layer samples with X-ray diffraction data. They concluded that the formation of the stoichiometric A15 phase (Nb_3Al) by a solid state reaction of thin Nb/Al multi-layers is basically determined by the intermediate formation of a metastable NbAl solid solution. They reported the formation of sigma phase (Nb_2Al) as well as Nb_3Al in the case of thick Nb/Al multi-layer samples (1000Å Nb / 307Å Al) after a heat treatment at 800°C/80 min.

Similar Nb/Al multi-layer samples have been made by sputtering at Lawrence Berkeley Laboratory to simulate the Nb/Al filament morphology of the wires. Multi-layer samples have the following advantages over powder metallurgy processed wire samples in studying reactions at the Nb/Al interface:

1) Precise control of layer thickness

2) Uniformity of layers

3) Homogeneous distribution of the Nb and Al layers

Transmission electron microscopy studies on these multi-layers can provide direct microstructural information which can not be obtained from x-ray diffraction techniques. This microstructural information about reactions at the Nb/Al interface will be used to determine optimum conditions for Nb/Al superconducting wire processing.

EXPERIMENTAL PROCEDURE

Nb/Al multi-layer samples were made by sputtering Nb and Al alternately on various substrates. 10~20 pairs of Nb/Al layers with thickness of 300Å Nb/80Å Al (No. 1) or 1000Å Nb/270Å Al (No. 2) were used for this experiment. An overall composition of 25 atomic% Al was desired for stoichiometric Nb_3Al phase formation. The actual layer thickness measurements correspond to 23 atomic% Al. Si wafers, Nb and quartz plates were used as substrates. An extra thick (2000Å) Nb layer was initially sputtered on the substrates to prevent undesired reactions between the multi-layers and the substrates.

Samples with thicker Al layers (No. 3) were made by cold rolling a stack of Al-coated Nb plates. The final configuration of Nb/Al layers is comprised of alternating 600Å thick Al layers and 0.5 mm thick Nb layers; the exterior Nb plates being covered by a thick layer of Al as shown schematically in Figure 4. It is not possible to control the Al thickness precisely in this way, but it is a straightforward method of producing Nb/Al layers of this thickness range. Details of these samples are given in Table 1.

Table 1. Layer configuration of samples

Samples	Thickness (Nb/Al)		Al
	desired	achieved	atomic %
No. 1	300Å/92Å	300Å/80Å	23 %
No. 2	1000Å/308Å	1000Å/270Å	23 %
No. 3	--	5000μm/0.06μm	
	--	5000μm/5000μm	

The samples were heat treated as shown in Table 2. TEM sample preparation was much easier with the Si-substrate than with the Nb-substrate; the Si substrate thinned faster than the Nb/Al multi-layer region. During the heat treatment at 600°C, the substrate Si reacted with the extra thick initial Nb layer, but did not affect Nb-Al compound formation. However for heat treatments at 900°C, only the Nb substrates were used in order to avoid any undesirable reaction with the substrates. An X-ray diffraction study is being undertaken using quartz plate substrate samples: these results will not be discussed in this paper.

Table 2. heat treatment conditions for the multi-layer samples

Samples	Heat treatments
No. 1, No. 2	600°C / 100 hrs , 900°C / 20 min
No. 3	600°C / 100 hrs (+ 900°C / 20 min)

A special technique has been developed to make cross-sectional TEM samples of these multi-layers. Samples glued together with sputtered sides facing each other were put into a 3 mm diameter brass tube before being sectioned to 50 mil thickness. The sliced samples were then mechanically thinned and dimpled until perforation. The samples were finally thinned by ion milling.

A scanning transmission electron microscope was used to identify the reacted compounds at the Nb/Al interface. Chemical analysis was done by EDX using 400Å size microprobe . A computer program was developed for indexing the micro-diffraction patterns from different phases.

RESULTS AND DISCUSSION

A series of Nb/Al multi-layer samples with an overall composition of 23 atomic% Al wsa made by sputter deposition. A cross-sectional view of the unreacted multi-layer samples is shown in Figure 1.

The results of heat treatments are identical for both samples No. 1 and No. 2. For heat treatments at 600°C, both samples showed $NbAl_3$ formation at the Nb/Al interface. In the case of sample No. 2, the $NbAl_3$ layer was about 350Å thick and the residual Nb layer was about 900Å thick as shown in Figure 2. Chemical analysis by EDX indicated that the $NbAl_3$ phase consisted of 75 atomic% Al and 25 atomic% Nb, while no noticeable Al solid solution was found in the residual Nb.

The resulting $NbAl_3$ and the residual Nb layers would be 345Å and 900Å thick if all of the Al was used to form stoichiometric $NbAl_3$ without forming a NbAl solid solution. This agrees with our experimental results. Conversely, if the 20 atomic% Al solid solution had formed, the resultant $NbAl_3$ and NbAl solid solution layers would have been 90Å and 1192Å thick, respectively.

Bormann et al.[12] reported that all of the Al was dissolved into a NbAl solid solution in the case of the 300Å thick Nb layers after a heat treatment of 2 hr at 700°C. The Al solution in Nb was calculated at 20~25 atomic% Al, by measuring a shift in the X-ray diffraction peak.

According to the Nb-Al equilibrium phase diagram[1], a NbAl solid solution of less than 10 atomic% Al is stable below 1000°C. Special quenching techniques must be used to suppress A15 formation from the supersaturated NbAl solid solution made at high

temperatures. NbAl solid solution will readily transform into compounds if diffusion is allowed. Therefore it is unlikely that Nb and Al would form a metastable solid solution of 20~25 atomic% Al during low temperature (≤ 700°C) heat treatments.

In the 900°C/20 min heat treatments performed in this study, all of the Al and Nb layers from samples No. 1 and 2 reacted to form the A15 phase (Nb_3Al) as shown in Figure 3. The A15(Nb_3Al) grains were equiaxed and approximately 1000~2000Å in size, similar to those typically found in powder metallurgy processed wires. The chemical composition was approximately 23 atomic% Al as predicted from the layer thickness ratio. Sigma phase (Nb_2Al) or residual Nb was not found in the reacted region. NbAl solid solution was not observed in the vicinity of the Nb/Nb_3Al interface.

It is concluded that one can avoid the Nb_2Al formation or residual Nb by controlling the Nb and Al layer thickness and distribution. Nb and Al layers as thick as 1000Å (Nb) / 270Å (Al) may react to form single phase A15(Nb_3Al).

The configuration of sample No. 3 can be divided into two separate regions as shown in Figure 4. Region 1 has Al and Nb layers which are thicker than 0.5 mm. Region 2 has alternating 600Å thick Al layers and 0.5 mm thick Nb layers. After the initial heat treatment at 600°C for 100 hrs, only $NbAl_3$ phase formed in the regions 1 and 2. NbAl solid solution was not found in the vicinity of Nb/$NbAl_3$ interface.

The $NbAl_3$ phase found in region 2 transformed into a mixture of A15(Nb_3Al) and sigma(Nb_2Al) after an additional heat treatment at 900°C for 20 min. The Nb_2Al phase formed a layer between two Nb_3Al layers as shown in Figure 5. The average grain size of the Nb_3Al was 1000~2000Å while that of Nb_2Al was only a few hundred Å, in agreement with the microstructure of the P/M wires. This Nb_3Al/Nb_2Al/Nb_3Al configuration is often found in the powder metallurgy processed Nb/Al wires (Figure 6).

Therefore we can argue as follows: for a region with an Al layer of 600Å thickness range, the Nb and $NbAl_3$ react to form A15(Nb_3Al) at the Nb/$NbAl_3$ interface as the first step in the reaction. Some of the Al in the $NbAl_3$ is consumed as the Nb_3Al forms.

When the Nb_3Al grains grow to form a continuous layer, the Nb diffusion is blocked and the remaining $NbAl_3$ between the two Nb_3Al layers becomes too lean in Nb to form Nb_3Al. As a consequence, sigma(Nb_2Al), the Nb poor phase, forms as the second step in the reaction. In the case of Nb/Al powder metallurgy processed wires, the Nb_3Al phase formation was observed for heat treatments above 700°C.

Region 1, however, has an infinite source of Al. Even after the heat treatment at 900°C for 20 min, only $NbAl_3$ was observed. The grains were equiaxed and embedded in the Al matrix as shown in Figure 7. It is likely that the $NbAl_3$ grains break out from the Nb/Al interface into the molten Al matrix due to the stress developed during the phase transformation.

The above observations indicate that sigma(Nb_2Al) and $NbAl_3$, as well as A15(Nb_3Al) can be thermodynamically stable at high temperatures and that the local composition determines which compound will form.

The reactions at the Nb/Al interface can be summarized as follows.

1) $Nb + Al \text{--------}> NbAl_3$

   - for below 600°C

2) $Nb + NbAl_3 \text{----}> Nb_3Al\ (+ Nb_2Al)$

   - at high temperatures (> 700°C)

   - Nb_2Al forms when the Al layer is much thicker than 270Å.

When the Al supply is infinite, only reaction 1) occurs even at high temperatures. NbAl solid solution was not observed on any occasion.

CONCLUSION

Reactions near the Nb/Al interface were studied in Nb/Al multi-layered samples using a TEM. A sample preparation technique was developed for cross-sectional observation of multi-layers with TEM. A computer program was developed to index micro-diffraction patterns.

Multi-layers with both 1000Å Nb/ 270Å Al and 300Å Nb/80Å Al layer ratios were reacted at 600°C for 100 hrs, resulting in the formation of $NbAl_3$ phase. The composition of the $NbAl_3$ was approximately 75 atomic% Al. A 900°C/20 min heat treatment resulted in complete reaction to the single phase A15(Nb_3Al) for the multi-layer samples No. 1 and 2. The composition of Nb_3Al was determined to be about 23 atomic% Al. NbAl solid solution was not observed in any samples or heat treatments used.

The Nb/Al Sample No. 3 transformed to the $NbAl_3$ phase at 600°C. This $NbAl_3$ layer reacted with Nb to form a layered $Nb_3Al/Nb_2Al/Nb_3Al$ configuration similar to that seen in the Nb/Al P/M wires, after the heat treatment at 900°C for 20 min. In the case of the 0.5 mm thick Al layer, however, only the $NbAl_3$ phase was observed regardless of heat treatment conditions. The $NbAl_3$ grains were equiaxed and embedded in the Al matrix.

The reactions at the Nb/Al interface are largely dependent on the configuration of Nb and Al layers as well as the heat treatment conditions. A15(Nb_3Al), sigma(Nb_2Al) and $NbAl_3$ can coexist at 900°C with the appropriate Nb and Al layer configuration. It is concluded that the sigma(Nb_2Al) and residual Nb can be avoided if the Nb and Al layers are thin and uniformly distributed with the proper atomic ratio. The Al layer should not be much thicker than 270Å in order to react to only A15(Nb_3Al) phase.

This information can be used to determine the optimum processing conditions for Nb/Al superconducting wires made by powder metallurgy.

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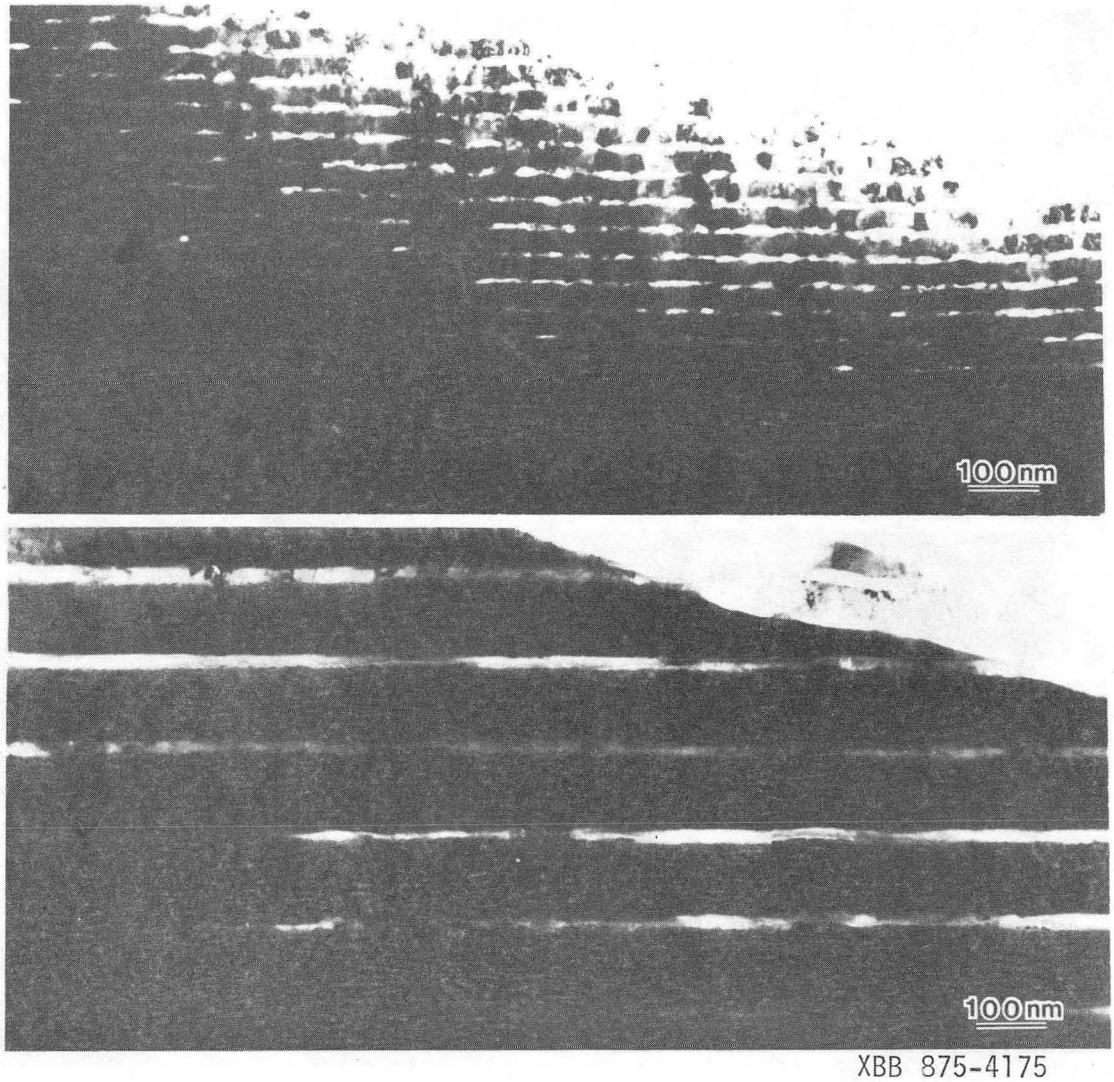

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Fig. 1 Cross-sectional view of unreacted multi-layer samples
(a) 300Å Nb/80Å Al (No. 1), (b) 1000Å Nb/270Å Al (No. 2)

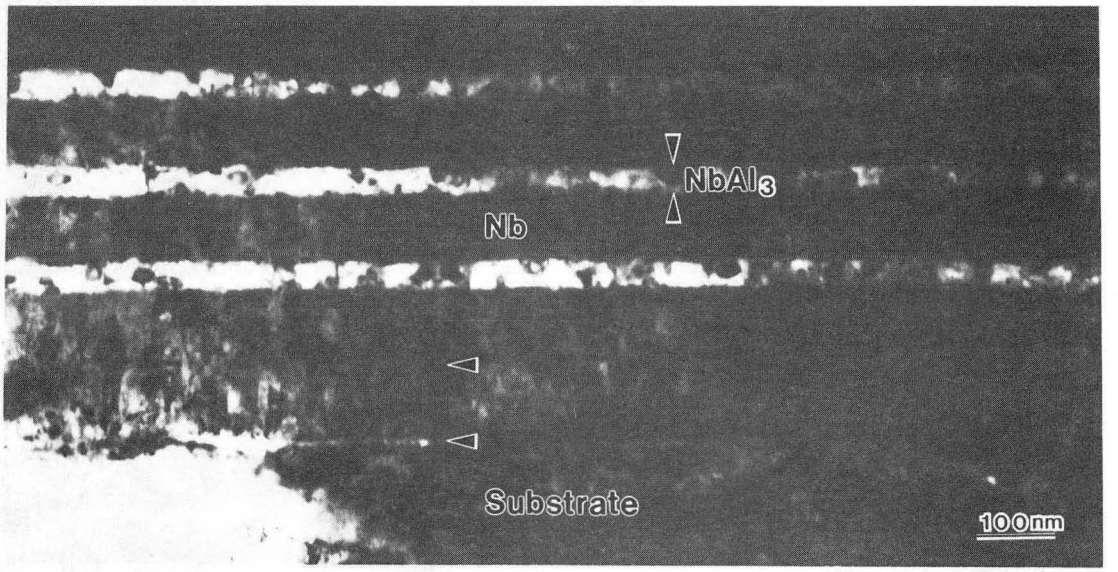

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Fig. 2 Sample No. 2 heat treated at 600°C/100hrs
The $NbAl_3$ layer is about 350Å thick and the left-over Nb is about 900Å thick. An extra layer of Nb is shown between arrows.

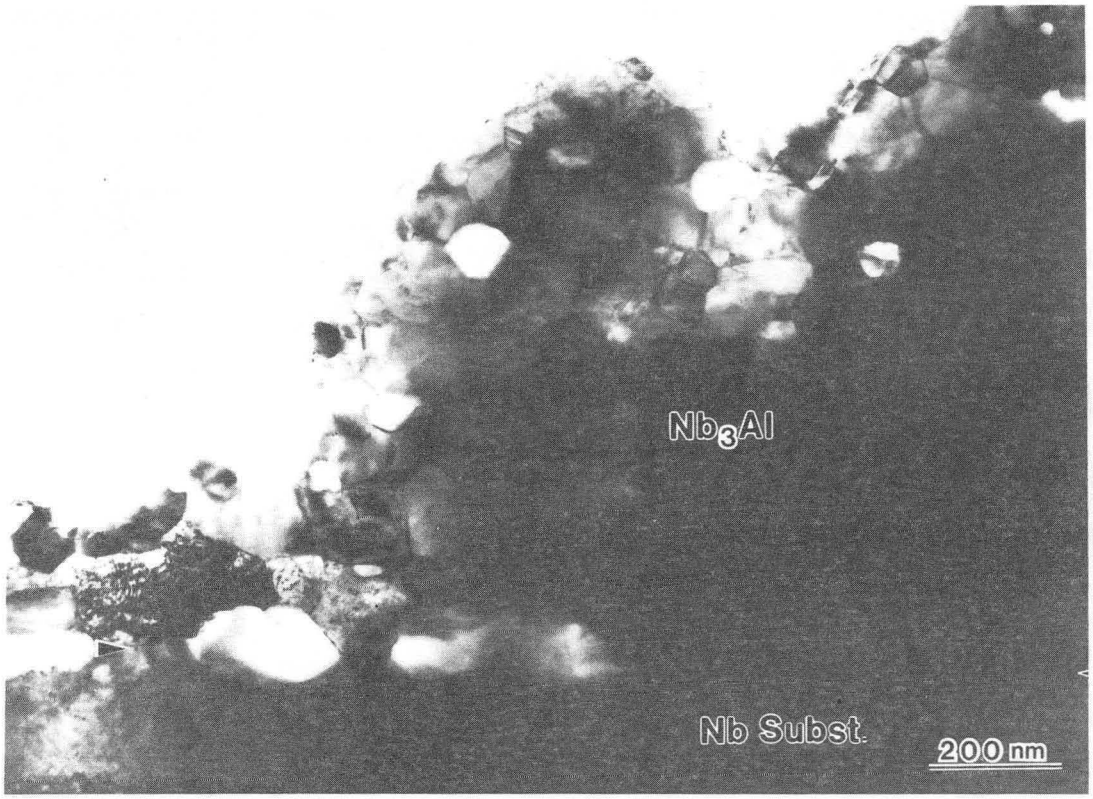

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Fig. 3 Sample No. 2 heat treated at 900°C/20min.
Single phase Nb_3Al (A15) has formed.

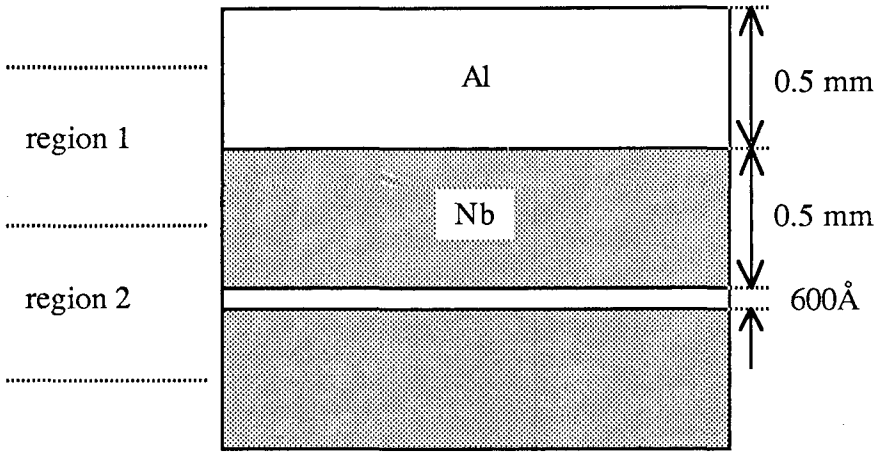

Fig. 4 Layer configuration of sample No. 3

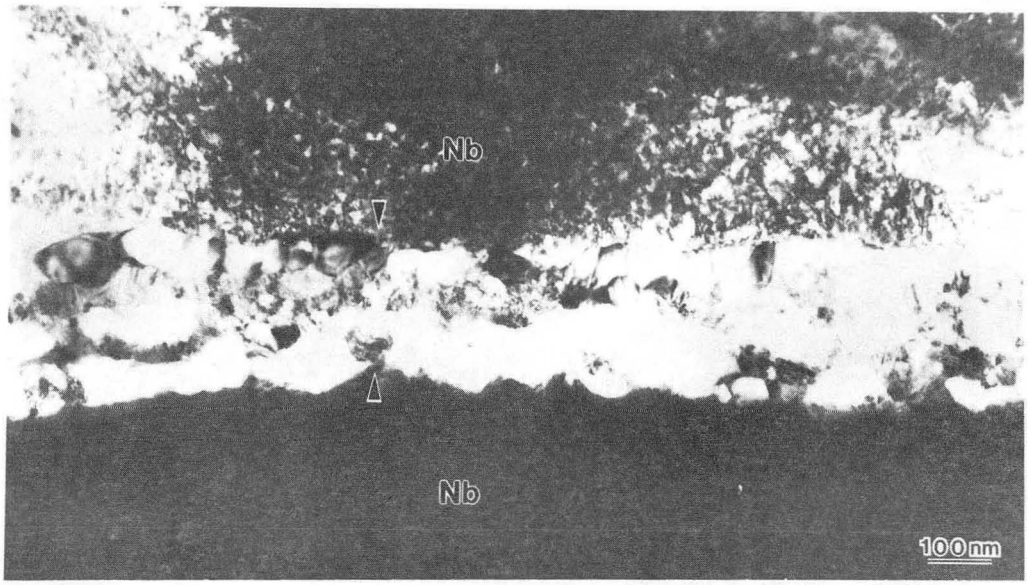

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Fig. 5 The $Nb_3Al/Nb_2Al/Nb_3Al$ layer is shown between the arrows in the region 2 of sample No. 3 (600°C/100hrs + 900°C/20min. heat treatment)

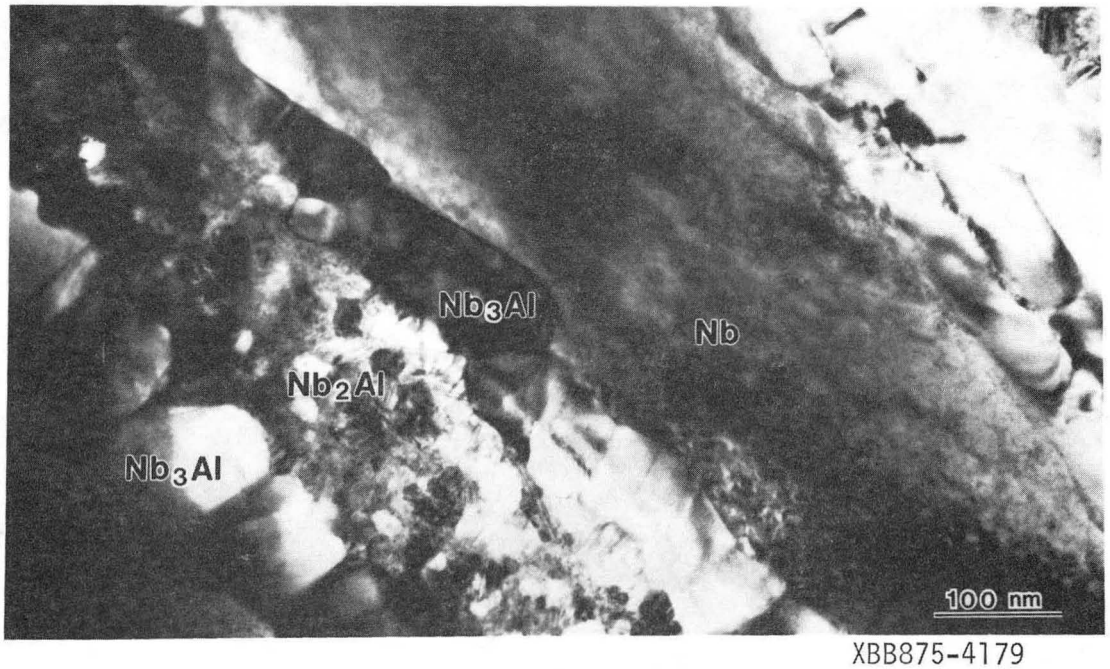

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Fig. 6 5 w% Al powder metallurgy processed Nb/Al wire sample heat treated at 900°C/20min.

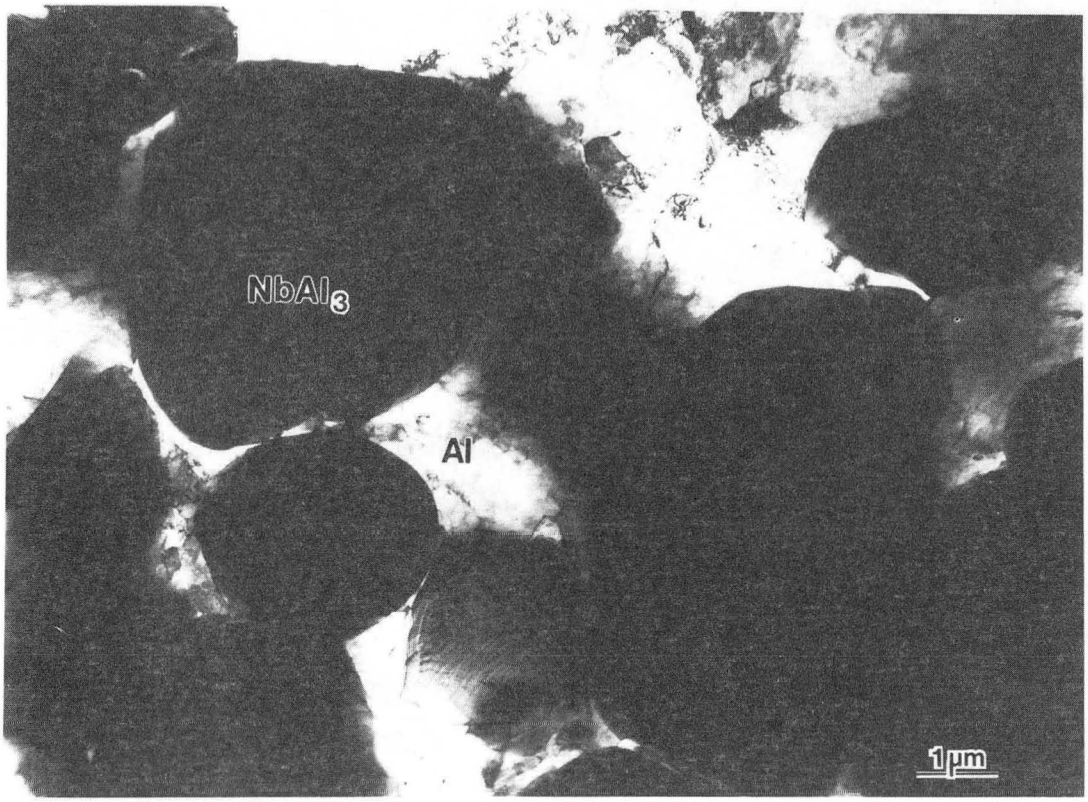

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Fig. 7 Region 1 of sample No. 3
heat treated at 600°C/100hrs + 900°C/20min.
Coarse $NbAl_3$ grains are shown embedded in Al matrix.

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