

# CORROSION BEHAVIOR OF Nb-BASE MATERIAL CONTAINING 24 wt% Sn at VARIOUS CHLORIDE CONCENTRATIONS

Gadang Priyotomo\* dan Pius Sebleku

Research Center for Metallurgy and Materials, Indonesian Institute of Sciences

Kawasan Puspiptek Gd.474, Setu, Tangerang Selatan, Banten, Indonesia

E-mail : \*gadangp@gmail.com

Masuk tanggal : 20-01-2015, revisi tanggal : 12-03-2015, diterima untuk diterbitkan tanggal : 19-03-2015

## Intisari

**SIFAT KOROSI DARI MATERIAL BERBASIS Nb YANG MENGANDUNG 24% BERAT Sn PADA BERBAGAI KONSENTRASI NATRIUM KHLORIDA.** Sifat korosi pada material berbasis Nb yang berisi 24% berat Sn yang terdiri dari fasa  $Nb_3Sn$  dan  $NbSn_2$  telah diinvestigasi dengan menggunakan pengujian polarisasi, potensiostatik dan metode analisis permukaan (SEM dan EDS) di dalam larutan netral NaCl. Pelarutan terseleksi pada fasa  $NbSn_2$  terjadi dengan konsentrasi rendah pada Nb dibandingkan dengan fasa  $Nb_3Sn$ . Melalui kurva polarisasi, rapat arus korosi dan laju korosi pada material meningkat dengan peningkatan konsentrasi klorida. Pada daerah pasif, pelarutan terseleksi tidak terjadi pada dua fasa yang ada, namun pelarutan tersebut terjadi di daerah transpasif. Peningkatan konsentrasi klorida memberikan efek mengganggu terhadap ketahanan korosi pada material. Hasil yang didapat juga menjelaskan efek galvanik antara fasa-fasa yang menyebabkan kelarutan terseleksi pada fasa  $NbSn_2$ .

*Kata kunci : Kelarutan terseleksi, Korosi, Konsentrasi klorida, Uji polarisasi*

## Abstract

**CORROSION BEHAVIOR OF Nb-BASE MATERIAL CONTAINING 24 wt% Sn at VARIOUS SODIUM CHLORIDE CONCENTRATIONS.** The corrosion behavior of Nb-base material containing 24wt% Sn that are consisted of  $Nb_3Sn$  and  $NbSn_2$  phases, has been investigated using polarization test, potentiostatic test and surface analytical method (SEM; scanning electron microscope and EDS; Energy Dispersive Spectroscopy) in neutral NaCl solutions. It was found that the preferential dissolution of  $NbSn_2$  phase with a lower Nb concentration compared to  $Nb_3Sn$  phase. From polarization curves, the corrosion current density and corrosion rate of the material increase with the increase of chloride concentration. In passive region, there is no preferential dissolution in both the phases, whereas the preferential dissolution of  $NbSn_2$  takes place in transpassive region. The increase of chloride concentration has detrimental effect in the corrosion resistance of the material. The results obtained were also explained the galvanic effect between the phases generating for the preferential dissolution of  $NbSn_2$  phase.

*Keywords : Preferential dissolution, Corrosion, Chloride concentration, Polarization test*

## INTRODUCTION

Niobium alloy are widely used in several corrosion-resistant applications such as rocket and jet engines, nuclear reactors, sodium vapor highway lighting, chemical-processing equipment<sup>[1-2]</sup>. Furthermore, niobium alloy exhibits excellent corrosion resistance in mineral acids, except in hydrofluoric acid, whereas in heavy corrosive solution, like concentrated acids and/or at high temperatures, this alloy is prone to take place corrosion attack<sup>[3]</sup>. On the other hand,

by adding Sn with certain concentration in Nb, it can create the intermetallic material like  $Nb_3Sn$  composing A15 phase<sup>[4]</sup>. This intermetallic material has a good superconductor property which generates magnetic fields over 12 T at temperature of 4.2 K<sup>[5]</sup>. In addition, due to remarkable superconductor property,  $Nb_3Sn$  intermetallic material has used in high energy physics (HEP), fusion energy applications such as the international thermonuclear experimental reactor (ITER), in chemical analysis in nuclear magnetic resonance (NMR) systems, and

in standard high field laboratory magnets<sup>[6]</sup>. Furthermore, the fabrication and further investigations on Nb<sub>3</sub>Sn intermetallic material already carried out widely<sup>[2,4-7]</sup>. Yamasaki and co-workers already investigated that by the reaction at 690°C Sn rich intermetallic material, NbSn<sub>2</sub>, was formed at first and transformed to Nb<sub>6</sub>Sn<sub>5</sub> next, and finally to Nb<sub>3</sub>Sn after 50 - 100 hours of heat treatment<sup>[7]</sup>.

Up to the present, Nb-base alloy containing Sn such as Nb<sub>3</sub>Sn and NbSn<sub>2</sub> intermetallic material have not systematically been investigated for corrosion behavior in aqueous solution. Furthermore, there is no particular investigation for the effect of other intermetallic material like the presence of NbSn<sub>2</sub> on the corrosion behavior of the Nb-base alloy containing Sn which has been conducted with previous researcher. Therefore, the purpose this work is to elucidate the corrosion behavior of Nb-base alloy with addition of 24 wt% Sn with various chloride concentrations at ambient temperature.

## EXPERIMENTAL PROCEDURE

### The specimens

Nb-Base alloy containing Sn consists mainly of 24 wt% Sn (tin) and 76 wt% Nb (niobium) was made by mixing the powders of Sn and Nb, compacting and heating at the temperature of 1173 K for the holding time of 96 hours. Furthermore, all specimens of alloy was made and manufactured by Firdiyono and co-workers from Research Center for Metallurgy and Material, Indonesian Institute of Sciences<sup>[8]</sup>.

### Polarization Test

The specimens were polished with silica carbide paper up to 1200 grit and then were rinsed with distilled water and cleaned in an acetone ultrasonic bath. The test solutions were neutral sodium chloride solutions with various chloride concentrations (0.0001 to 0.1 kmol/m<sup>3</sup>),

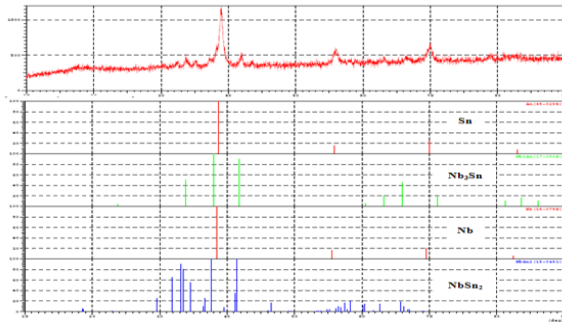
which were made with the distilled water and high grade chemical reagent. The test temperatures used was at ambient temperature. The polarization experiments were carried out in a round bottom cell of 1000 ml capacity using a potentiostat apparatus (Reference 600, Gamry Instrument), interfaced to a personal computer. The potential values were measured by using a reference electrode of a saturated calomel electrode (SCE). All potentials referred in this work are with correspond to SCE for the reference electrode. The surface of the working electrode was covered with epoxy resin to expose a test area of 0.6 cm<sup>2</sup>. A platinum wire served as the counter electrode. Prior to polarization and potentiostatic tests, the open circuit potential (OCP) was monitored and the experiments were begun after the stabilization of OCP for 1 hour. Furthermore, all the data were duplicated to ensure reproducibility of the results. Those experiments were carried out at a scan rate of 0.167 mV/s. After and before conducting the experiments, the morphology and distributed elements of the specimen surface were investigated and observed by using scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDS).

## RESULTS AND DISCUSSION

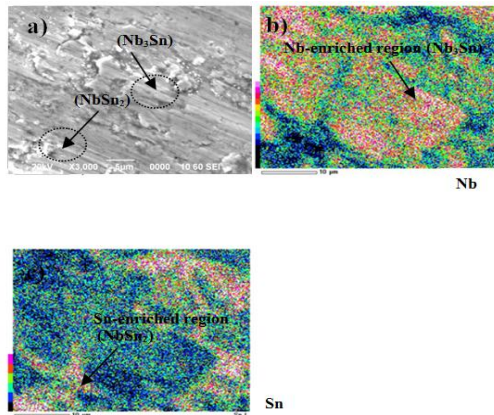
### Microstructure of material

The structure of the Nb-base material containing 24 wt% Sn was determined by x-ray diffraction (XRD). Firdiyono and co-worker had already investigated and elucidated the pattern of XRD for this material, where the material of present work is the same sources with them<sup>[8]</sup>. The observed reflections can be indexed as the Nb<sub>3</sub>Sn and NbSn<sub>2</sub> phases, where the rest ones are Nb and Sn. Furthermore, Figure 2 shows that element distribution in the surface of Nb-base material containing 24 wt% before corrosion test. The Nb-enriched region and Sn-enriched region were indicated as Nb<sub>3</sub>Sn and NbSn<sub>2</sub> phases

respectively. However, the presence of Nb and Sn which lies on the materials are neglected.



**Figure 1.** The x-ray diffraction pattern of the Nb-base material containing 24 wt% Sn<sup>[8]</sup>

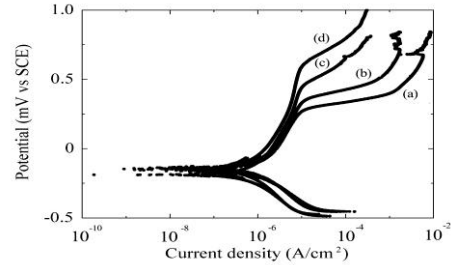


**Figure 2.** Element distribution in the surface of Nb-base material containing 24 wt% before corrosion test. (a) SEM image, (b) Nb and (c) Sn

### Polarization Curve and The Effect of Chloride Concentration

Figure 3 shows polarization curves of Nb-base material containing 24 wt% Sn in various chloride concentration at ambient temperature. These curves were divided by two regions such as anodic polarization curve and cathodic polarization curve. The anodic polarization curve of this material shows that the magnitude of anodic current densities increases with increasing chloride concentration. Furthermore, these curves show that the ranges of passive regions are more wider with decreasing chloride concentration. The passivating film begins to break down in passive region in higher anodic potential. An oxygen evolution starts to take place with the sudden

increase in anodic current. On the other hand, the magnitude cathodic current densities also increase with increasing chloride concentration.



**Figure 3.** Polarization curves of Nb-base alloy containing 24 wt% Sn in (a) 0.1 M; (b) 0.01 M; (c) 0.001 M and (d) 0.0001 M NaCl solutions at ambient temperature

Table 1 shows corrosion potential ( $E_{\text{corr}}$ ), corrosion current density ( $i_{\text{corr}}$ ) and corrosion rate (CR) of Nb-base material containing 24 wt% in various neutral sodium chloride at ambient temperature. These parameters obtained by tafel polarization method. This method is corresponded to rate of an electrochemical reaction to the over potential. On the basis of present work, the increase of chloride concentration could increase the magnitude of corrosion potential, corrosion current density and corrosion rate respectively. However, at 0.001 M NaCl solution, the corrosion potential ( $E_{\text{corr}}$ ) is slightly higher than 0.0001 M NaCl solution. Alvarez and co-worker elucidated that the smoother surface had higher corrosion potential<sup>[9]</sup>. It means that the corrosion potential moves to active region due to rougher surface of specimen.

**Table 1.** Corrosion potential ( $E_{\text{corr}}$ ), Corrosion current density ( $i_{\text{corr}}$ ) and Corrosion rate of Nb-base material containing 24 wt% in various neutral sodium chloride at ambient temperature

Concentration (M)	$E_{\text{corr}}$ (mV vs SCE)	$i_{\text{corr}}$ (A/cm <sup>2</sup> )	CR (mpy)
0.0001	-145	6.03E-07	1.886
0.001	-188.1	5.91E-07	1.847
0.01	-140.5	7.51E-07	2.349
0.1	-152.3	8.76E-07	2.739

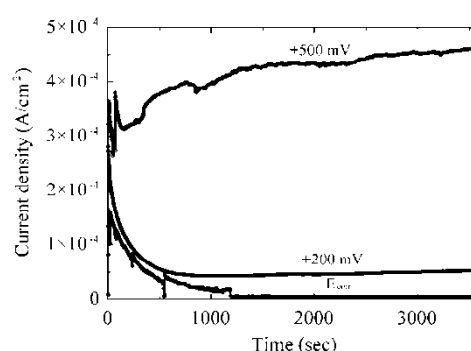
On the basis of present work, the corrosion current density and corrosion rate of the material increase with the increase of sodium chloride concentration. Therefore, the increase of sodium chloride concentration has detrimental effect for Nb-base material containing 24wt% Sn.

### Potentiostatic Test

The potentiostatic method of polarization has the benefit that it can follow more closely the behaviour of metals during the formation and breakdown of passivating films. Figure 4 shows a potentiostatic test of Nb-base material containing 24 wt% Sn at the potentials of  $E_{\text{corr}}$ , +200 mV and +500mV vs (SCE) as a function of exposure time in 0.1 M NaCl solution at ambient temperature. This figure elucidates the current fluctuations of the materials at various constant potentials such as  $E_{\text{corr}}$ , +200 mV and + 500 mV vs SCE. These results, like all the current fluctuations reading for the material, were taken after 3600 seconds of immersion. At  $E_{\text{corr}}$ , the sharp decrease in the current density with the function of time take places up to 1300 seconds. During decreasing in the current density, the current fluctuated at certain interval of time. It means that the anodic reaction took place on the particular surface of material during occurrence of repassivation process on the surface. From the exposure time of 1300 seconds, the current density stabilized, where no fluctuated current occurred.

On the other hand, at +200 mV vs SCE, the common feature of this plot is that a large current density is initially observed due to a combination of double layer charging, and the current density moves to a stable value as well as austenitic stainless steel 316L<sup>[10]</sup>. In addition, the constant potential of +200 mV vs SCE in the potential range of passive region is shown in Figure 3. In passive state, the oxide commonly spreads over the surface to form a thin film. The passage of metal ions through an oxide film takes place very

slowly and so the current due to metal ions leaving the metal becomes very small. Furthermore, the surface is completely covered with an oxide film. The author suggests that the possible formation of oxide film take place both Nb<sub>3</sub>Sn and NbSn<sub>2</sub> phases in passive region. If current spikes were occurred, the magnitude of these spikes would have higher intensity. However, for this material, there is no evidence for the metastable pitting due to no current spikes except for 14 wt% Cr duplex stainless steel<sup>[11]</sup>.



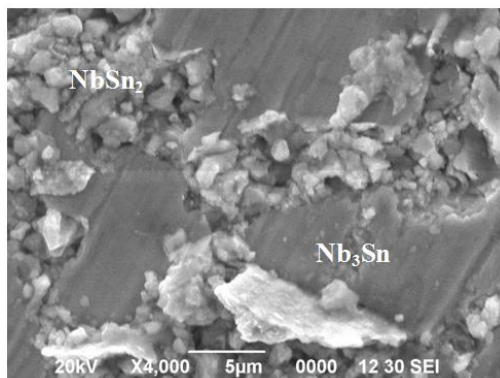
**Figure 4.** Potentiostatic tests of Nb-base material containing 24wt% Sn at the potentials of  $E_{\text{corr}}$ , +200 mV and +500 mV vs (SCE) as a function of exposure time in 0.1 M NaCl solution at ambient temperature

Furthermore, at +500 mV vs SCE, this condition is higher than that of passive condition at +200 mV vs SCE. The current density increases sharply, which means that the dissolution of passive film took place in transpassive region. In addition, for high anodic potentials, the oxygen evolution occurs that the film must be conduct electronically<sup>[12]</sup>.

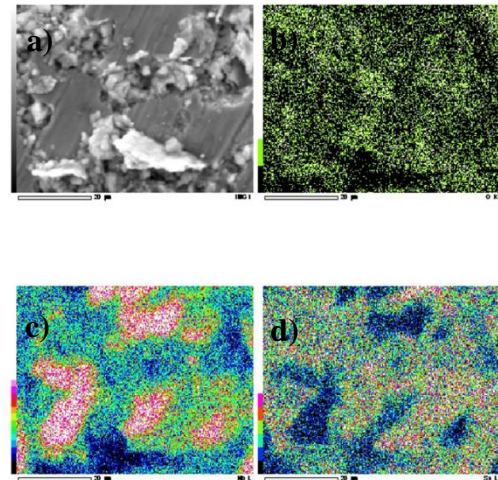
### The preferential dissolution of NbSn<sub>2</sub> phase

Figure 5 shows that Nb-base material containing 24 wt% Sn has the preferential dissolution of Sn-enriched phase such as NbSn<sub>2</sub> compared to Nb-enriched phase such as Nb<sub>3</sub>Sn. Furthermore, this suggest that Nb-base material 24 wt% Sn has a different corrosion behavior between Nb<sub>3</sub>Sn and NbSn<sub>2</sub> phases, in a sense that

$\text{Nb}_2\text{Sn}$  phase has apparently a lower corrosion rate than  $\text{Nb}_3\text{Sn}$  phase. In addition, under the polarization condition, the difference in the anodic current density between these phases cannot be elucidated by the preferential dissolution. It is assumed that the presence of  $\text{NbSn}_2$  phase would lead to the increase in the anodic current density, comparing with  $\text{Nb}_3\text{Sn}$  phase. A further experiment must be carried out to describe in detail. On the other hand, the author considers that the preferential dissolution of  $\text{NbSn}_2$  phase from the amount of Nb in this phase is shown in Fig.6. The amount of Nb was found to be more enriched in  $\text{Nb}_3\text{Sn}$  than in  $\text{NbSn}_2$  phase, which means that the former film has a larger dissolution rate than that of the latter film. In addition, the other consideration is the enrichment of Nb has less active than that of Sn<sup>[12]</sup>. It means that the phase consists of the enrichment of Nb as the cathode compared to that of Sn as the anode. The presence of cathode and anode side on  $\text{Nb}_3\text{Sn}$  and  $\text{NbSn}_2$  indicate to contribute the difference of potentials for both of these materials as well as  $\text{Ni}_3(\text{Si,Ti}) + 2\text{Mo}$ <sup>[13]</sup>. In addition, the difference of potentials of materials take place galvanic corrosion<sup>[13]</sup>. Therefore, it implies that the preferential dissolution of  $\text{NbSn}_2$  phase took place due to galvanic effect between  $\text{NbSn}_2$  and  $\text{Nb}_3\text{Sn}$  phases.



**Figure 5.** Microstructure of Nb-base alloy containing 24wt% Sn after corrosion test in 0.1 M NaCl solution at ambient temperature



**Figure 6.** Element distribution in the surface of Nb-base material containing 24 wt% Sn after polarization test for in 0.1 M NaCl solution at ambient temperature. (a) SEM image, (b) O, (c) Nb and (d) Sn

## CONCLUSION

The corrosion behavior of Nb-base material containing 24 wt% Sn in various chloride concentrations has been studied. The following things were obtained.

1. The corrosion current density and corrosion rate of the Nb-base material containing 24 wt% increase with the increase of sodium chloride concentration.
2. The increase of sodium chloride concentration has detrimental effect in the corrosion resistance of the material.
3. Nb-base material 24 wt% had the preferential dissolution of  $\text{NbSn}_2$  phase with a lower Nb concentration compared to  $\text{Nb}_3\text{Sn}$  phase in sodium chloride solution.
4. The galvanic effect between the phases generates the preferential dissolution of  $\text{NbSn}_2$  phase.

## ACKNOWLEDGEMENT

The author is grateful to Dr. Firdiyono and co-workers of Research Center for Metallurgy and Materials, Indonesian

Institute of Sciences for their useful support in providing the material

## REFERENCES

- [1] ASTM Committee., 1987. ASM Metals Handbook Vol.13 Corrosion. In: Corrosion of Niobium and Niobium Alloy, T.L., Yau and R.T. Webster, ASM International, United State of America, pp: 1874-1882. ISBN 0-87170-007-7 (v.1).
- [2] Miyazaki, T., Miyatake, T., Kato, H., Zaitso, K., Murakami, Y., Hase, T and Hamada, M. 2008.,Development of Nb<sub>3</sub>Sn superconducting wires for high field magnets at Kobe Steel and JASTEC". *Cryogenics* 48 : 341–346.
- [3] Robin, A. 1997.,Corrosion Behavior of Niobium, Tantalum and their Alloys in Boiling Sulfuric Acid Solutions". *International Journal of Refractory Metals & Hard Materials* 15 : 317-323.
- [4] Sumption, M.D., Bhartiya, S., Kovacks, C., Peng, X., Gregory., E., Tomsic, M.J and Collings, E.W. 2012.,Critical Current Density and Stability of Tube Type Nb<sub>3</sub>Sn Conductors". *Cryogenics* 52 : 91-99.
- [5] Tachikawa, K., Natsuume, M., Kuroda, Y and Tomor, H. 1996.,Critical current density and stability of Tube type Nb<sub>3</sub>Sn Conductors". *Cryogenics* 36 : 113-117.
- [6] Godeke, A., Den Ouden, A., Nijhuis, A and Ten Kate, H.H.J. 2008.,State of Art Powder-in-Tube Niobium-Tin Superconductors". *Cryogenics* 48 : 308-316.
- [7] Yamasaki, H and Kimura, Y. 1982.,Fabrication of Nb<sub>3</sub>Sn superconductors by the solid-liquid diffusion method using Sn rich CuSn alloy". *Cryogenics* : 89-98.
- [8] Firdiyono, F. 2010.,Pembuatan Kawat Superkonduktir Nb<sub>3</sub>Sn dengan Metoda Nano-Powder-In-Tube untuk aplikasi Kumparan Magnet". Laporan akhir Kumulatif Kegiatan Kompetitif LIPI.
- [9] Roxanna B. Alvarez , Holly J. Martin , M.F. Horstemeyer, Mei.Q. Chandler, Neil Williams, Paul T. Wang, Augusto Ruiz. 2010.,Corrosion relationships as a function of time and surface roughness on a structural AE44 magnesium alloy". *Corrosion Science* 52 : 1635–1648.
- [10] Meng, Guozhe., Yuan Li, Yawei Shao, Tao Zhang, Yanqiu Wang, Fuhui Wang.2013.,Effect of Cl<sup>-</sup> on the Properties of the Passive Films Formed on 316L Stainless Steel in Acidic Solution". *Journal of Materials Science & Technology*: 1-6.
- [11] Garfias-Mesias, L.F., J.M. Skykes. 1999.,Metastable Pitting in 14 Cr Duplex Stainless Steel". *Corrosion Science* 41: 959-987.
- [12] Stephen D. Cramer and Bernard S. Covino, Jr. 2003. ASM Handbook, Volume 13A, Corrosion: Fundamentals, Testing, and Protection: 42-51. ISBN: 0-87170-705-5.
- [13] Priyotomo, G., Okitsu, K., Iwase, A., Kaneno, Y., Nishimura, R. and Takasugi, T. 2011.,The Corrosion behavior of Intermetallic Materials Ni<sub>3</sub>(Si,Ti) and Ni<sub>3</sub>(Si,Ti) + 2Mo in Acidic Solutions". *Applied Surface Science*, 257(19): 8268-8274.