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A Study on interfacial activities between Nb and liquid Al in static and dynamic condition

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Abstract

In the present study, an effort has been made to investigate the interfacial activities between the solid Niobium and liquid Aluminium. Aluminium was melted at 750 ºC temperature and subsequently, solid niobium was immersed into the liquid aluminium and held for different time intervals. The study was conducted in static as well as dynamic conditions. Temperature and time were similar for both static and dynamic conditions. After solidification, the Nb-Al interface was studied under optical microscopy, scanning electron microscopy, EDS and X-Ray diffraction analyzer. The analysis revealed that there was no change in the dimension of Nb sample and no intermetallic compound formed on the surface or subsurface of solid Niobium under present experimental condition.

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Keywords: *Phase transformation; Diffusion; Intermetallic compound; Microhardness; Niobium; Aluminium;*

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1. Introduction

The interest in high-temperature inert metals all across the periodic table is increasing as their uses enhance in some critical areas. Technical developments in the past several decades have focused on uncommon metals such as Nb, V, Mo, Zr, etc. However, these materials are rare and costly, and very narrow information has been recorded on their potential as a useful metal [1]. For several engineering applications and different operating environments including elevated temperature application, Nb is a suitable material [2]. Also, Nb is a body-centered cubic (BCC) material and it possesses properties like high melting point along with modest mass density, good biocompatibility, high ductility, and decent corrosion resistance [2,3]. However, high-purity niobium has a limited application where higher mechanical strength is needed as it is very soft in nature [2]. Due to its superior property in special conditions, Niobium has attracted the interest of many researchers recently. Niobium is used as an ultrasonic probe by several researchers [4]. Oxide of niobium is very stable and it has a melting point of 1400°C which makes it a refractory metal. The diffusion of aluminum into the surface of niobium is also one of the supreme auspicious methods to increase oxidation resistance. The phase diagram of the Nb/Al system generally has three intermetallic compounds. It was further observed the formation of the Nb_3Al at a higher temperature of 750°C[1,3]. The growth of Nb_3Al observed as a part of $Nb/Nb_3Al/Nb_2Al/NbAl_3$ phases in accordance with the phase diagram[5]. Dahlgren et al stated that the formation of the Nb_3Al phase effectively in the temperature range 550–850°C [5–7]. Later they had reported that the formation of the Nb_3Al phase occurs at the temperature above 650ºC [8]. And Vandenberg et al. reported Al_3Nb formation to occur above 750°C [9].

Carlson et al. [3] studied the behavior of the formation of Al_3Nb layer in Nb surface at a higher temperature and oxidation behavior of Nb and its alloy which suggests a parabolic growth of the Al_3Nb in Nb and found the rate of formation of Al_3Nb per cm^2. T. Ogurtani further studied the diffusion rate and the growth kinetics of Al_3Nb formation in Al/Nb dynamic system condition at the variable time and temperature, they also suggested an equation to find the diffusion rate of Nb in the liquid Aluminum system by varying the time and temperature[1,3].

The intermetallic phase formed due to the immersion of Nb in dynamic condition was also observed by T. Ogurtani et al[3]. It was observed that diffusion starts at a very short duration of time. It was also shown that a layer of Al_3Nb phase formed in the layer of the sample. There are very few pieces of literature available on Nb and Al interfacial activities. Due to its high-temperature usability, niobium is of interest for many the researcher in some critical application, for example, Ultrasonic probe, stirrer, etc., [10] as a replacement of ceramic material which is very brittle in nature and hard to reuse. In this study, a high-temperature study of pure Nb in pure liquid Al system in static and dynamic condition for the different intervals of time has been carried out to understand the phase formation and the effect of the same on the microstructural changes.

2. Experimental Procedure:

The sample of 10 mm x 12 mm x 12 mm has been prepared from the Pure Niobium (99.9%) bar. The samples were polished and cleaned before dipping into liquid Al melt. 200 gm of commercially pure Aluminium was used for melting. Al was melted in a pit type furnace at 750ºC. For the dynamic test conditions, Nb sample was supported in a tungsten wire as tungsten is non-reactive at the operating temperature with both Al and Nb. Thereafter, tungsten wire was supported in a shaft driven by an electric motor. Nb sample was then dipped in liquid aluminium and stirred at a constant speed of 1000 rpm for the different intervals of time 10 min, 20 min 30 min and 60 min. After the experiment, the samples were taken out and cleaned for further analysis. In the case of the static condition, the Nb sample was dipped in molten aluminium for a similar time interval as dynamic test condition and hold for the said time interval. Henceforth, the sample cooled inside the aluminium were subjected to interface studies. Light Optical Microscope (LOM) as well as Scanning Electron Microscope (SEM), Oxford-energy dispersive X-ray were employed to characterize the microstructure of the samples. Furthermore, in order to check intermetallic phases, X-ray diffractometer (XRD) with PanAnalytical X’ Pert Powder with Cu (K_α) radiation has been done. The experimental parameter has been illustrated in table 1.

Table 1. Experimental parameter

Condition	Holding Time (min)	Temperature **(°C)**	Rotation Speed (rpm)	Cooling Process
Static Condition	10 20 30 60	750	Static	Dipped for mentioned time frame and solidified in an open environment inside the crucible.
Dynamic Condition	10 20 30 60	750	1000	Held for the mentioned time frame and solidified in open air by cleaning stuck aluminium from Nb.

3. Results and Discussion:

Fig. 1 and 2 are the optical images of the static and dynamic sample for 10 min, 20 min, 30 min, and 60 min respectively. For the static sample with 10 min of holding, it is clear that Al and Nb don't have any common interface, which is evident by a perfect gap between the two surfaces[Fig. 2]. Likewise, as the timeframe increases 20 min to 60 min, there is no significant difference between the structure. For the dynamic sample (Fig. 2), with holding time of 10 min, Nb sample shows a clear microstructure that has no evidence of any intermetallic compound. The same phenomena continued as the time frame increases from 20 min to 60 min.

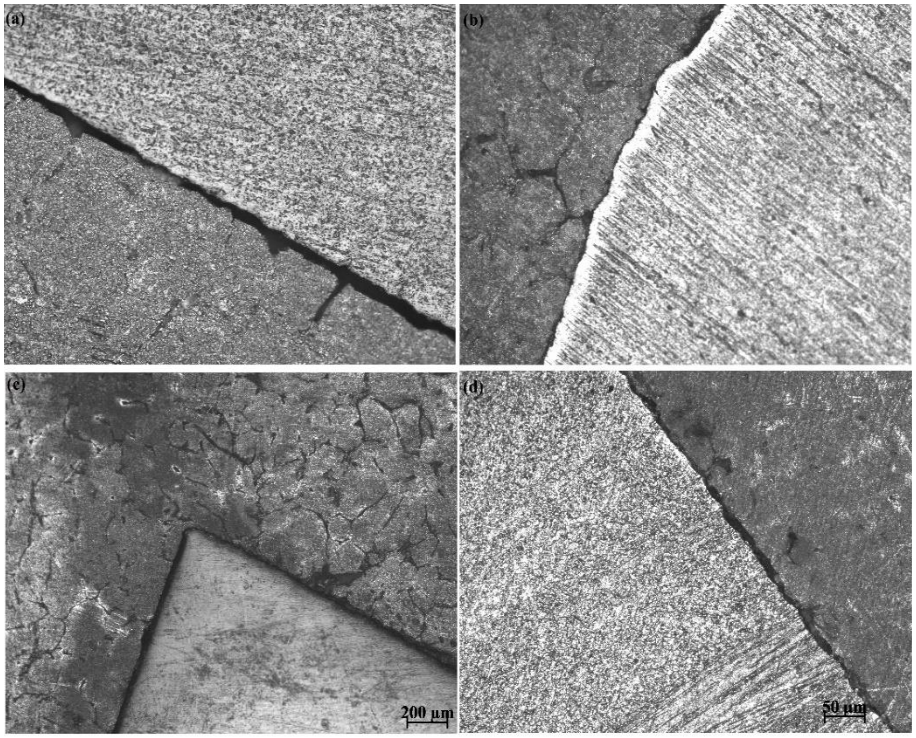


Fig. 1. Optical microstructure of the static sample for different time frame (a) 10 min holding (b) 20 min holding (c) 30 min holding (d) 60 min holding

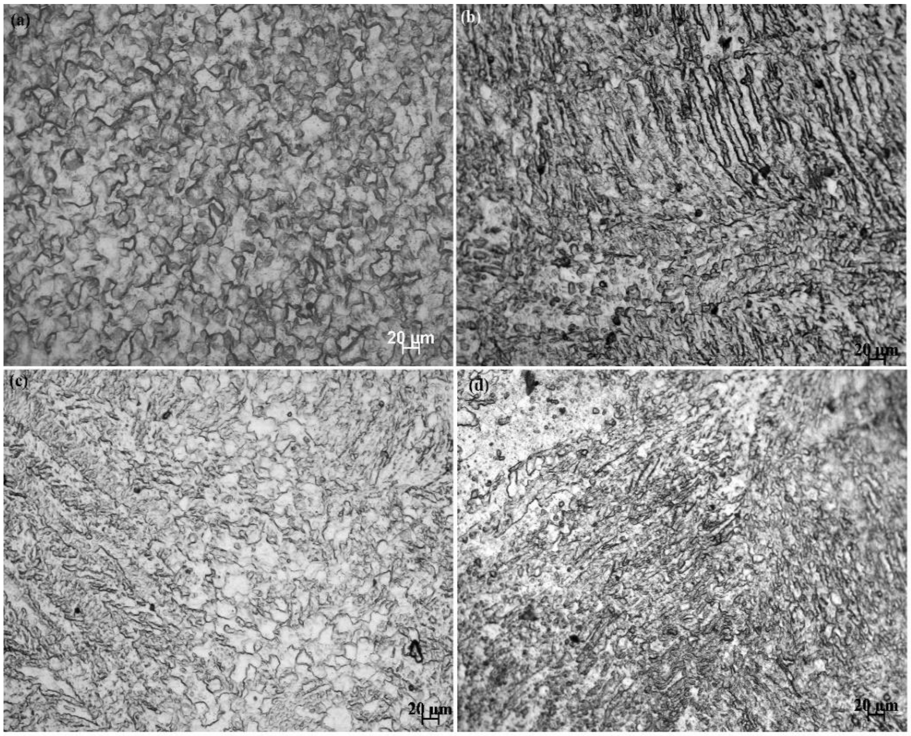


Fig. 2. Optical microstructure for dynamically rotated Nb Sample for different time frame (a) 10 min holding (b) 20 min holding (c) 30 min holding (d) 60 min holding

For the further validation of the effect of Al in the Nb sample, EDS of all static and dynamic sample has been performed. Fig. 4 and 5 shows line mapping of the Al/Nb static sample and EDS result of the dynamically rotated Nb sample respectively. It is clear from the line mapping of static sample which was solidified together (Fig. 3 (a)), the interface has no evidence of Al and Nb. The same mechanism also observed on 20, 30 and 60 min samples. However, from the analysis of the Electron diffraction spectroscopy(EDS) of dynamically rotated sample for all the condition Fig. 4(a-d), it has been observed that there is no mark of Al penetration on Niobium sample which implies that there was no intermetallic compound formed during the present operational time and temperature period.

Fig. 5 (a-b) shows the XRD pattern by implying the static and dynamic samples (10 min, 20 min, 30 min, 60 min). XRD analysis was carried out with PanAnalytical high score plus software. Fig. 5(a) shows the XRD pattern of the static sample which shows FCC structure of Al and BCC structure of Nb. Fig. 5 (a and b) also indicate that there is no diffraction pattern matching Al_3Nb phase or any other intermetallic compound in both static and dynamic conditions. Hence, in the present experimental conditions. Nb may not form an intermetallic compound with Al in present experimental conditions.

As explained in the phase diagram of Al and Nb, three intermetallic compounds (Al_3Nb, $AlNb_3$, and $AlNb_2$) forms due to the diffusion of Al in Nb [10,11]. Diffusion largely depends upon time and temperature. In the present study, operational time is a maximum of 60 min and the temperature is 750°C. However as explained by the other reported literature [3], 800°C was the minimum operating temperature, where a phase named Al_3Nb was found on the surface of Nb[12,13,15]. T. Ogurtani observed the formation of Al_3Nb at a temperature of 800 ° C and they proposed an analytical approach to find diffusion rate for different temperature and time frame.

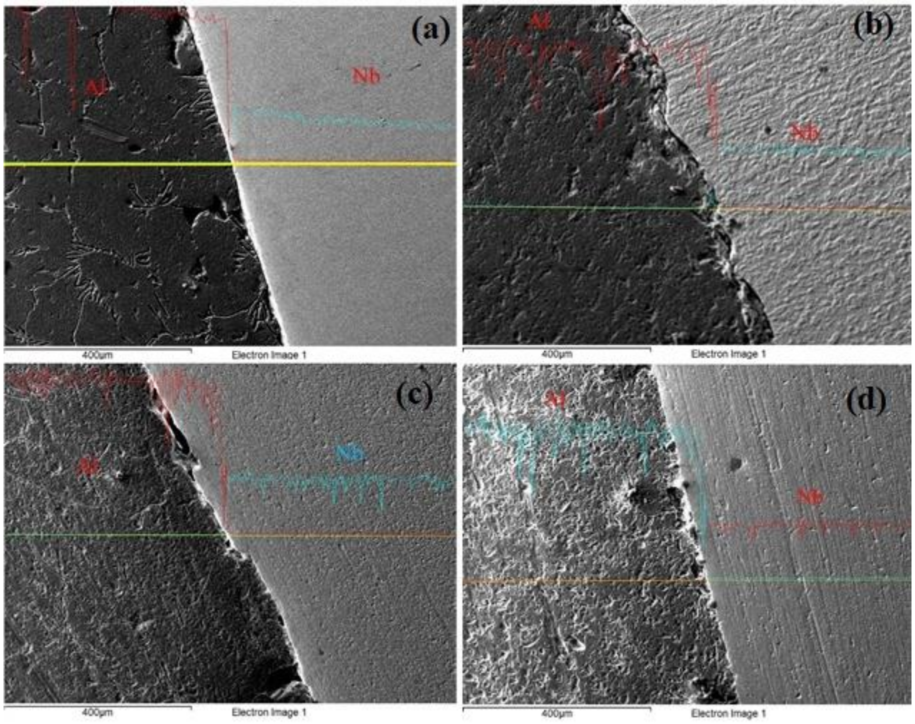
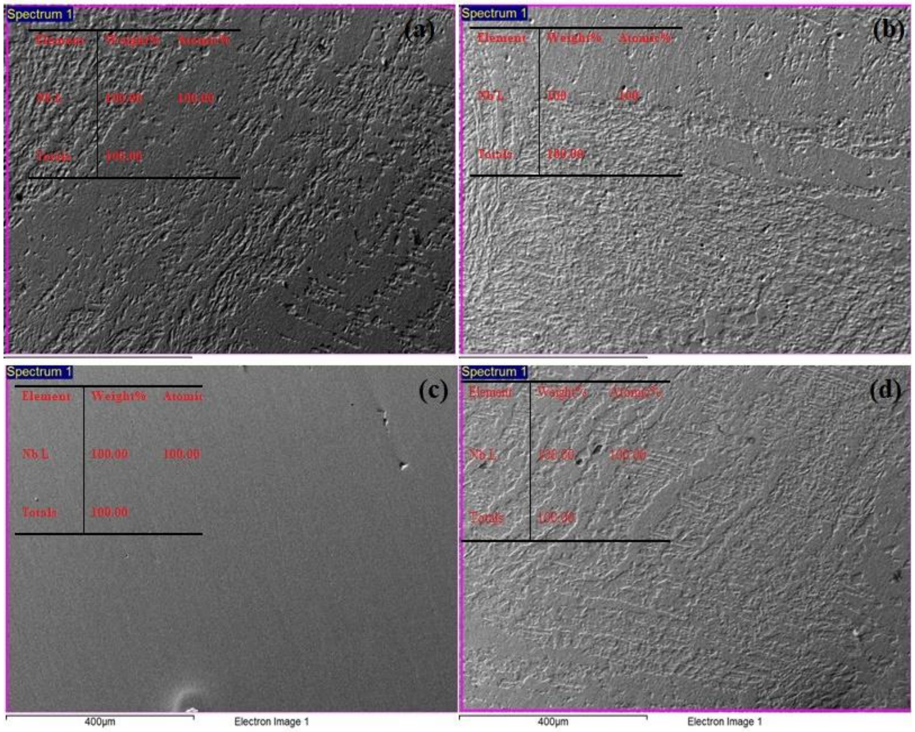


Fig. 3. Line mapping of the Al/Nb static sample for different time frame (a) 10 min holding (b) 20 min holding (c) 30 min holding (d) 60 min holding



(a)

Element	Weight%	Atomic%
Nb L	100.00	100.00
Totals	100.00	

(b)

Element	Weight%	Atomic%
Nb L	100	100
Totals	100.00	

(c)

Element	Weight%	Atomic
Nb L	100.00	100.00
Totals	100.00	

(d)

Element	Weight%	Atomic%
Nb L	100.00	100.00
Totals	100.00	

Fig. 4. EDS of the dynamically rotated Nb sample for different time frame (a) 10 min holding (b) 20 min holding (c) 30 min holding (d) 60 min holding

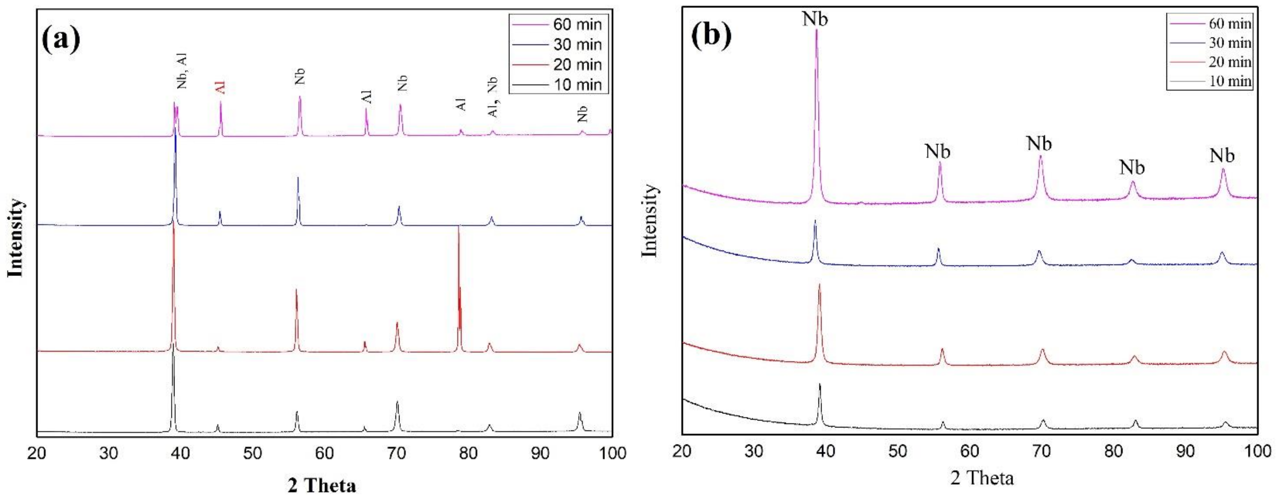


Fig. 5. XRD pattern of (a) Al/Nb Static condition (b) dynamically rotated Nb sample

Assuming that the Arrhenius relationship holds true as claimed by T.Ogurtani, we have the following relationship,

$$k = k_0 exp\left(\frac{-Q}{RT}\right) \text{----------------(eq. 1) [3]}$$

Where k is the rate constant, k_0 the preexponential factor, Q the activation energy, and T the absolute temperature. T.Ogurtani employed an analytical method to calculate Q and k_0 where Q , is 36.5 kcal per mole and k_0 is 5.4 sq. cm per sec[3].

Using the above values and using the theoretical value of R to be 1.9872 Cal/K. mol, rate constant k was calculated from eq. 1,

$$k = 5.4 \exp\left(\frac{-36.5\times10^3}{1.9872\times1023}\right) \quad \Rightarrow k = 8.60 \times 10^{-8} \text{ sq. cm per sec.}$$

In phases with very low component solubility, where the concentration of the diffusing element remains practically unchanged through the layer (i.e. Al_3Nb), the diffusion parameter (δD) can be found out in terms of the parabolic rate constant by means of relation;

$$(\delta D) = \frac{3k}{8} \text{-------------(eq. 2) [3]}$$

Where D is the interdiffusion coefficient in the layer, δ is the gradient over the whole phase field. By using the value of k from eq. 1,

$$(\delta D) = 3.22\times 10^{-8} \text{ sq. cm per sec.}$$

As claimed by T.Ogurtani [3], the reactive diffusion taking place on the surface of niobium obeys parabolic kinetics and can be expressed by the following relationship,

$$h^2 = k.t \text{--------------(eq. 3) [3],}$$

Where h is the thickness of probable Al_3Nb phase may form, k is the parabolic rate constant, and t is the diffusion-annealing time.

Hence, if in this research work, if probable Al_3Nb phase form at 750ºC then the phase thickness has been calculated theoretically by using eq. 3.

For t = 10 min.$\Rightarrow h = (0.007185\ cm) \Rightarrow h = (71.85\mu m)$

Similarly, for t = 20 min. $\Rightarrow h = (0.010162\ cm) \Rightarrow h = (101.62\ \mu m)$

For t = 30 min. $\Rightarrow h = (0.012446\ cm) \Rightarrow h = (124.46\mu m)$

For t = 60 min. $\Rightarrow h = (0.017601 cm) \Rightarrow h = (176.01\mu m)$

Fig. 6 shows the graphical representation of the diffusion thickness for the different holding time frame with the theoretically observed values. It has shown a linear increment of the diffusion thickness as time increases.

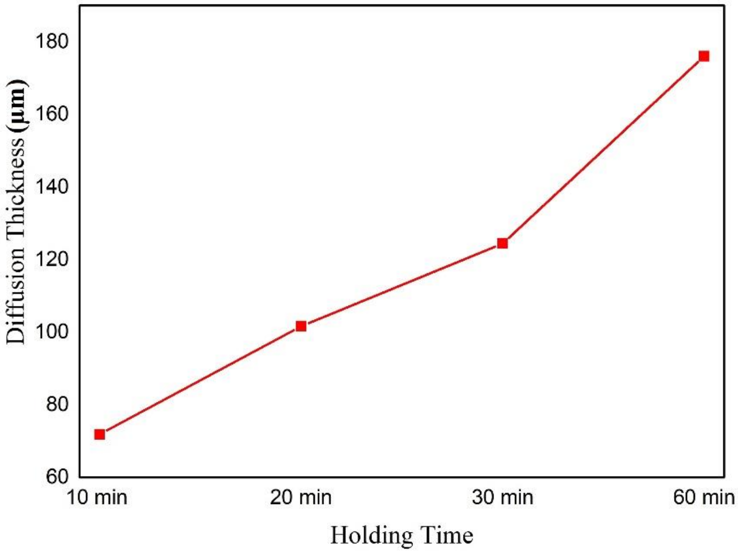


Fig. 6. Graphical representation of the diffusion thickness for the different holding time frame

Though, a perfect gap between Nb and Al surface has been observed in Fig. 2 (static condition). Which shows poor wettability between Nb and Al at 750°C. This will restrict diffusion at Al-Nb interface in the present condition. Al has a melting point of 660°C and mostly used at an operating temperature range of 680-750 °C. From this study, it can be concluded that at a maximum temperature of 750°C, Nb can be deep in the molten Al which results in no diffusion and reaction. For the stirring and cavitation treatment (Ultrasonic probe, Stirrer blade) of Al, Nb can be used below 750°C.

4. Conclusion:

The thermal, chemical and physical stability of Niobium has been observed up to a temperature range of 750°C for a studied time frame of 60 min maximum in molten Al. It can be inferred from the optical microstructural analysis, SEM, EDS, and line mapping analysis that no other intermetallic compound has formed on the sample. This has been further confirmed form XRD pattern analysis which shows no other diffraction pattern except pure Aluminium and Nb. Hence, Diffusion and formations of intermetallic compounds were not observed during the static and dynamic test condition which confirms that Nb can be used in the liquid aluminium environment below 750°C.

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