

Oxidation of niobium and of niobium coated with aluminium in steam-air mixtures

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Niobium coated with aluminium oxidised in air at 650 °C.

SUMMARY.

The oxidation behaviour of pure niobium and of niobium coated with aluminium has been studied in the temperature range of 400 to 600 °C in different atmospheres: superheated steam of 1 atm., a mixture of steam and air, and in air.

Depending on temperature and on oxidation rate the following oxides have been found: NbO, NbO₂ needles, mixtures of NbO₂, and T Nb₂O₅ and a T Nb₂O₅ scale. The NbO₂ phase not only is formed below 500 °C and at low oxygen pressures, as reported in the literature, but also at high oxidation rates in air up to 600 °C.

The rate of oxidation is determined by the properties of the different oxides. Below 600 °C the Nb₂O₅ formed in air is a loose powder and formed in steam and steam+air is a rather dense oxide. The Nb₂O₅ scale flakes off at cooling down to room temperature. The NbO₂ needles furnish a better adherence of oxide to metal than do NbO₂ and Nb₂O₅. This may be due to a network formed by NbO₂ which is continued in the Nb₂O₅ phase.

The rate of oxidation of aluminium coated niobium in steam, steam+air and in air is alike when the temperature does not exceed 600 °C. A non-porous layer of NbAl₃ gives a reasonable protection. At temperatures higher than 600 °C two types of failures have been observed :

- oxidation of aluminium between NbAl₃ grains and
- formation of cracks in the NbAl₃ layer as a result of diffusion and thermal stresses. Once a crack has reached the metal substrate oxide is formed between metal and NbAl₃ layer.

It has been observed that the oxidation resistance is high at temperatures of about 1100 °C in air. On cooling, however, cracks are formed which destroy the oxidation resistance of aluminium coated niobium.

OXIDATION OF NIOBIUM

Introduction

It is only since the last few years that application of niobium has become more widespread. The applications are a result of several favourable properties: high melting point (2415°C), low specific weight, corrosion resistance against many acids, low neutron capturing cross section, good cold mouldability and good warm strength. An unfavourable factor is its tendency to oxidise easily.

The oxidation of niobium is rather complex. There are several forms of oxides and the oxidation is parabolic or linear, this being dependent on the temperature, the oxygen pressure and time of oxidation.

Table 1. Properties of the oxides.

	Lattice	Parameter		Microscopic appearance in	
		a	c	Non polarised light	polarised light
T-Nb ₂ O ₅				grey	Active
NbO ₂	Tetr.	4.84	2.99	grey	Non-active
NbO	Cub.	4.203		white	Non-active
NbO _x	Tetr.	3.387	3.274	Not distinguishable from niobium	
NbO _z	Tetr.	6.645	4.805	Needles	active

Table 1 gives the oxides already known together with their specific properties. According to Estulin [1] only the gamma and alpha modification of Nb₂O₅ exist; the oxide M Nb₂O₅ should be a mixture of gamma and alpha Nb₂O₅. Besides these oxides there are also NbO₂, NbO, NbO_x and NbO_z. The NbO_x and NbO_z occur in a niobium which is strongly supersaturated with oxygen.

According to Norman [2] these oxides are formed at low oxygen pressures and relatively low temperatures. The NbO_z oxide is precipitated as plates along the (110) planes of the niobium, which crystallises in a b.c.c. lattice. NbO_z gives a bright reflection in polarised light. NbO_x cannot microscopically be distinguished from niobium. The suboxide NbO_x appears to have optical properties very close to those of the metal niobium. According to Ståhl [2] the NbO_z has the composition NbO, whereas according to Kühner [2] NbO_x has a composition that lies between Nb₅O and Nb₆O.

Hurlen [3] oxidised pure niobium at different oxygen pressures. Initially the oxidation reaction proceeds linearly, then parabolically again linearly and finally parabolically. Hurlen gives the following reasons for this :

1. In the first linear part the oxygen on the surface is adsorbed and subsequently dissolved in the niobium surface. The activation energy for this stage is 14,7 kcal./Mol. The rate of oxidation is proportional to the square root of the oxygen pressure. Therefore, it is concluded the dissolution reaction is rate determining.
2. The oxygen, which is dissolved in the niobium surface, diffuses now deeper into the niobium. This stage has a higher activation energy, 27,4 kcal./Mol., and this agrees well with that of oxygen diffusion in pure niobium, determined with relaxation measurements.
3. The oxidation is linear and the activation energy is again 14,8 kcal./Mol. This low activation energy indicates a surface reaction. In this stage, the suboxide as well as a thin layer of Nb₂O₅ are formed. Nb₂O₅ originates here so easily due to oxygen vacancies in the suboxides.
4. The parabolic action is due to a thicker white stoichiometric Nb₂O₅. When the Nb₂O₅ layer becomes too thick it flakes off in accordance with the great Pilling and Bedworth relation (2,68) and the difference in the expansion coefficient.

If the oxidation takes place at high oxygen pressures it is possible that the first two stages are not found as the niobium surface is quickly saturated with oxygen.

For this reason Kolski [4] never found the first two stages since he oxidised in air and oxygen of 1 atmosphere. The oxidation products that arose were in all cases Nb₂O₅, NbO and the suboxides NbO_x

and NbO_2 . The existence of NbO_2 has not been strictly proven by Kolski but it is highly probable since Hurlen has found it. It also has been found in this investigation.

Experimental

Niobium was tested in superheated steam, a mixture of steam and air, and in air. The oxidation was carried out at 1 atmosphere total pressure. The steam was superheated by passing it through a furnace. The steam was cooled so that there was almost no water loss. The test pieces (12 X 7 X 3 mm) were placed in this superheated steam.

Oxidation rate

The specimens were weighed, every 24 hours. In the figures 1, 2 and 3 the results of these tests can be seen.

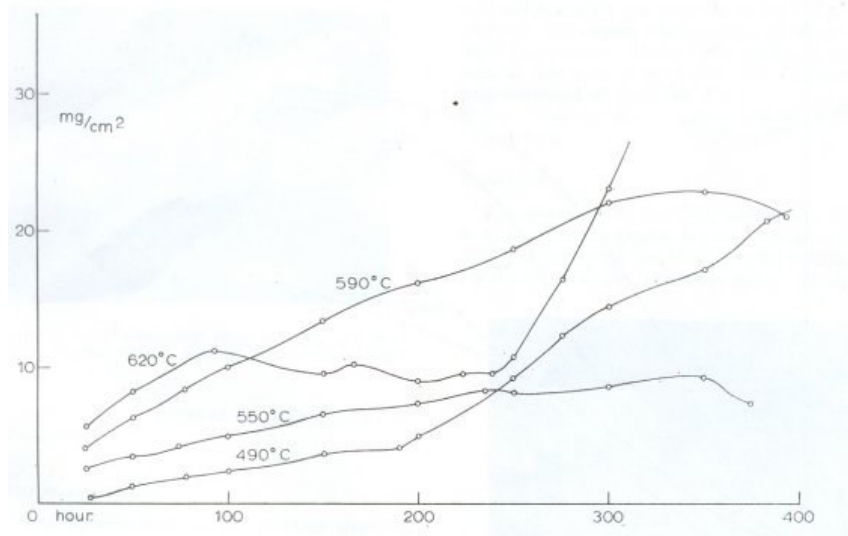


Figure 1. Corrosion of niobium in steam.

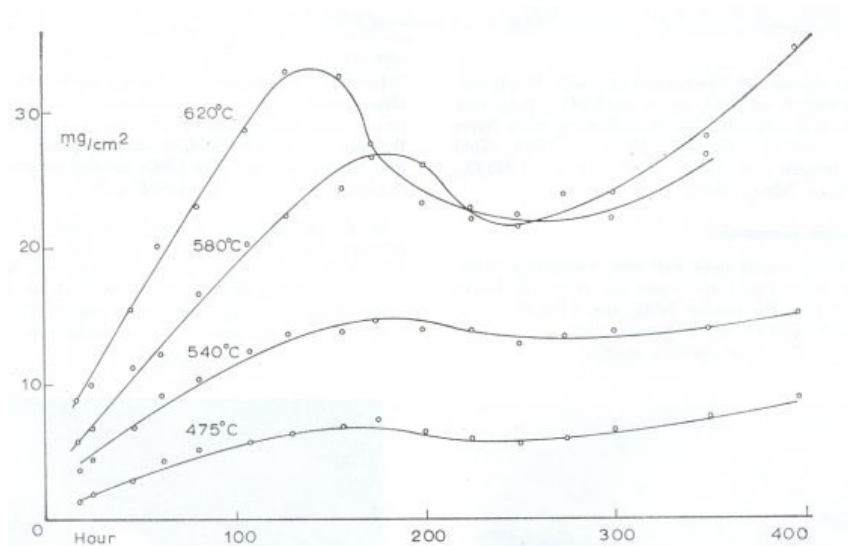


Figure 2. Corrosion of niobium in steam and air mixtures

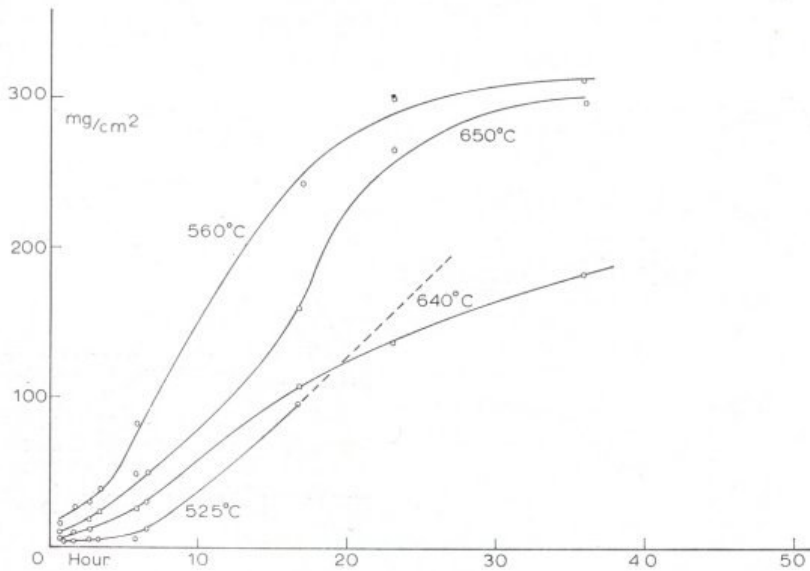


Figure 3. Corrosion of niobium in air.

Only a linear and a parabolic stage have been found. In the linear stage a grey surface was formed. In the parabolic stage the surface was white and the oxide cracked off at regular intervals. The linear stage here should be considered as the third stage of Hurlen's investigation.

In the lower temperature range the break-away appears sooner than in the higher temperature oxidation.

In the higher temperature oxidation the oxide cracks before the accelerated oxidation appears. One then finds a weight loss before the accelerated oxidation is found.

Upon oxidation in air the rate is at lower temperatures greater than at higher temperatures. Below 575 °C a very fine powdery $T-Nb_2O_5$ results. This powder is not found in the case of oxidation in steam and air-steam mixture. The Nb_2O_5 is here more sintered and there is little difference in the appearance of the specimens oxidised at different temperatures.

Röntgenographical analysis.

The oxidation products have röntgenographically been analysed. The X-ray reflections of the several oxides can overlap each other. The number of reflection lines of each oxide has been determined after polishing away some surface layers.

Table 2 gives a summary of the lines found for oxidation at temperatures lower than 525 °C. It is seen that a maximum occurs in the number of lines of NbO_2 and that on nearing the niobium the number of NbO_2 lines increases. When oxidised at 600 °C no NbO_2 occurs but NbO appears (see table 3) .

Table 2. After oxidation at 500 °C

Grinding	T- Nb_2O_5	Number of reflection angles found	
		NbO_2	NbO_z
0	13	4	1
1	7	14	7
2	7	14	8
3	3	6	11

Table 3. After oxidation at 600 °C

Grinding	T-Nb ₂ O ₅	Number of reflection angles found		NbO
		NbO ₂	NbO ₂	
1	13	12	2	2
2	9	16	8	8

It is concluded that the following oxide layers exist:

at 600 °C: T-Nb₂O₅, T-Nb₂O₅ + NbO₂ and NbO

at temperatures lower than 525 °C: T-Nb₂O₅, T-Nb₂O₅ + NbO₂ and NbO₂.

Microscopic examination.

The above results agree well with microscopic observations. Here also three layers are observed. Under polarised light the needles NbO₂ and T-Nb₂O₅, reflect whilst the NbO and the in-between layer composed of Nb₂O₅ and NbO₂, is optically inactive.

In steam and steam-air oxidation at a temperature above 550 °C only a NbO layer arises (Figure 4a) and below 500 °C NbO₂ needles (Figure 4b). Between 500 °C and 550 °C occurs a transition of NbO₂ into NbO (photo 4c). The NbO₂ needles become wider changing continuously into a NbO-scale.

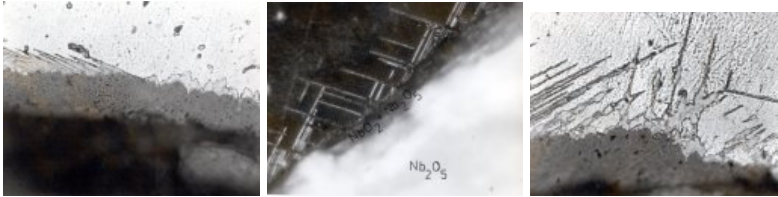


Figure 4a. By oxidising at 525 °C NbO. needles and the white uniform NbO-scale occur together. Non polarised light

Figure 4b. Polarising NbO. needles growing from the Nb.O. layer into niobium. Polarised light.

Figure 4c. The transition phase of NbO₂ and NbO. The NbO₂ needles become broader. Non polarised light.

In air oxidation NbO₂ needles are also formed at temperatures higher than 500 °C for instance, at 575 °C. This is in contradiction with the results of Norman who assumed that NbO₂ only occurred at low oxygen pressures and at a temperature below 500 °C. The NbO₂ is probably formed here because the niobium is supersaturated with oxygen as a result of the powdery nature of the T Nb₂O₅ in this case.

Hardness measurements.

Hardness measurements in the niobium near the NbO₂ needles and the NbO-scale show that the hardness near the NbO₂ is much higher than near NbO (Figure 5).

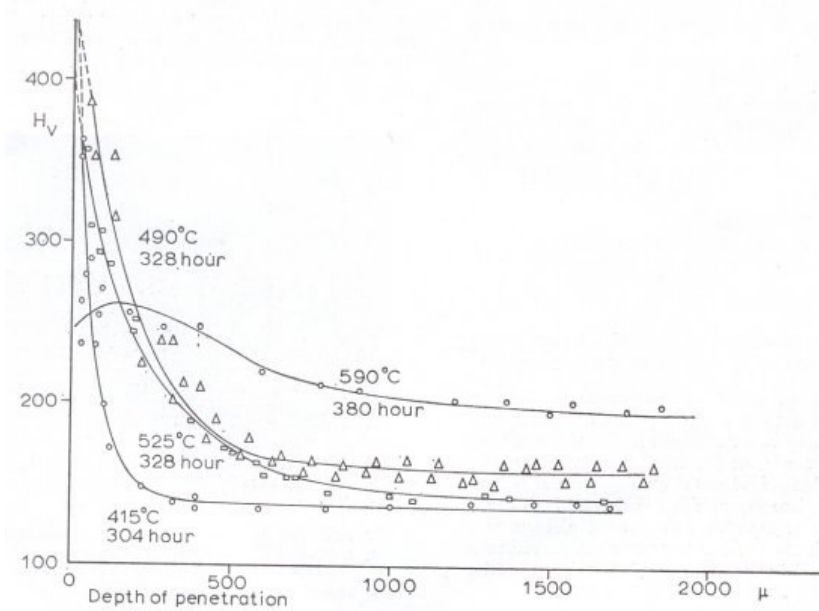


Figure 5. Hardness measurements of niobium specimens corroded in steam.

When the needles become broader and change into NbO the hardness decreases. This indicates that the contamination with oxygen in the regions where the intermediate phase of NbO₂ and NbO has precipitated is smaller than in areas where NbO₂ has precipitated. The oxygen contamination of the niobium at high temperatures, where NbO results, is much less than at the lower temperatures. The hardness in the neighbourhood of the NbO declines as a consequence of the withdrawal of the oxygen from the niobium during cooling.

Discussion.

The appearance of the NbO₂ needles and NbO-scale is in accordance with the measured oxidation rate curves. It is likely that the NbO₂ needles are responsible for the fact that the break-away occurs quickly at low temperature and that there is no weight loss for this accelerated oxidation. In Figure 6 it is seen that the pattern of the NbO₂ needles, as it were, is continued into the Nb₂O₅. The needles « pin » the Nb₂O₅ so that the surface layer upon cooling doesn't burst off.

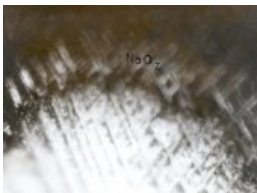


Figure 6. The NbO₂ needles pin the outside Nb₂O₅ scale; polarised light,

The NbO, however, does not possess this ability to « pin » the Nb₂O₅. NbO has a simple cubic lattice, so it can be expected that it is easily deformed. The Nb₂O₅ layer upon cooling easily flakes off from the NbO-scale.

The NbO₂ has no protective property at all so the Nb₂O₅ oxide can quickly grow.

Conclusion.

The results of the oxidation of niobium may be summarised as follows :

Three oxide layers are present :

1. An outside layer consisting of T-Nb₂O₅ which is a white, polarising oxide. The Nb₂O₅ is formed in layers except in air-oxidation, where it appears as a powdery oxide.
2. An in-between layer, consisting of T-Nb₂O₅ + NbO₂. This layer is non-polarising.
3. NbO₂ or NbO. NbO₂ is formed by oxidation in air below 575 °C as a result of rapid supersaturating of niobium with oxygen, whereas it occurs in steam oxidation below 500 °C on account of a low oxygen pressure. NbO is formed, when niobium is oxidised in air above 600 °C and in steam and steam-air above 550 °C.

The flaking of the Nb₂O₅ layer and the transition of the oxidation rate can be connected with the presence of the NbO₂ needles and the NbO-scale. The NbO₂ needles pin the Nb₂O₅. The break-away occurs sooner when NbO₂ needles are present because generally they are less protective than NbO.

OXIDATION OF NIOBIUM COATED WITH ALUMINIUM

Introduction.

It has been attempted to improve the corrosion resistance of niobium by alloying or applying a coating.

Some niobium alloys have improved resistance to oxidation but not sufficient for practical use. It appears that the valency and the atomic radius of the alloying element have a great influence. Optimum corrosion results are obtained when the alloying element is trivalent. The explanation of this has not yet been given. It is not to be expected that alloying niobium with another single element improves very much the resistance to oxidation. Therefore an oxidation resistant coating is sought. One good example of a coating is the Zn coating developed by Meussner [5].

Niobium and zinc give several different metallic compounds: NbZn, Nb₂Zn₃, NbZn₂ and NbZn₃. Upon oxidation a protective layer of ZnO is formed. If this layer is damaged the NbZn₃ is oxidised and NbO₂ is formed whilst zinc evaporates. This zinc is oxidised and the damage is repaired. Carlson tested the behaviour of an AlSi coating. He used an Al/Si 15 % alloy that was applied by the dipping method. According to Carlson [6] no self-healing occurs but thermal changes do not cause damage to the coating. Carlson, however, does not state any reason why this coating is not completely satisfactory nor does he explain which reaction mechanism takes place. The oxidation mechanism of a pure aluminium coating on pure niobium was investigated in order to elucidate the factors causing failures.

Experimental

The dipping

The niobium was dipped in molten aluminium. The most effective conditions appeared to be at 970 °C during 10 minutes. The niobium was then fully covered with aluminium except on the corners and edges. Due to the long dipping time also a layer of NbAl₃ with inter-crystalline aluminium is formed.

Thus, the coating exists of a layer of aluminium and between the aluminium and the niobium a layer of NbAl₃. The other inter-metallic compounds Nb₂Al and Nb₃Al were not formed upon dipping. This was also tested with the aid of the microscan-analyser. The NbAl₃ layer has not a dense structure, but much inter-crystalline aluminium is present. It is even possible that the aluminium is « sucked » in the NbAl₃ since upon formation of NbAl₃ from niobium and aluminium there has to be a shrinkage of 8 % (Figure 7). These aluminium coated niobium specimens were tested in superheated steam of 1 atm.



Figure 7. Aluminium canals formed during dipping of niobium in molten aluminium.

The oxidation in steam at low temperatures (400-600 OC).

The oxidation is very irreproducible and, of course, depends upon the quality of the coating. In places where $NbAl_3$ is present and no free aluminium the $NbAl_3$ is oxidised to a niobate $xNb_2O_5 \cdot yAl_2O_3$. The niobium under the niobate never seemed to oxidise.

Thus, this niobate can be considered as having a protective effect. However, the niobium oxidises locally where the coating has been damaged. The resulting Nb_2O_5 pushes the coating away and the oxidation then proceeds increasingly faster (Figure 8).

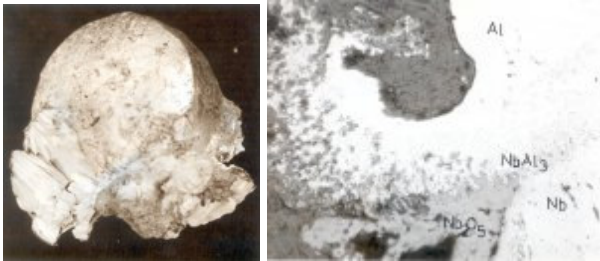


Figure 8. The $NbAl_3$ coating is pushed away by the formation of Nb_2O_5 .

The coating can break in the two following ways:

1. The oxidation of the aluminium in-between the NbAl_3 . Above 650 °C the aluminium is oxidised rapidly into a white powdery Al_2O_3 . At lower temperatures this oxidation was not observed. Probably the rate of oxidation was too low. In case there is an aluminium canal through the NbAl_3 , as can be seen on Figure 7, the coating will be broken locally and the underlying niobium will oxidise.
2. Cracking of the coating. Cracks in the coating seemed to occur at temperatures above 605 °C after some time had elapsed. The occurrence of these cracks can be closely correlated to the following results:
 - Cracks are only formed in the dense NbAl_3 . This may happen upon dipping, but usually by diffusion a dense NbAl_3 layer is formed during the oxidation. (Figure 9a).
 - Below 605 °C no cracks occur and no dense NbAl_3 is formed during the oxidation at these temperatures.
 - Sometimes the cracks continue into the niobium as shown in the Figure 9b.
 - Cracks are inter- and trans-crystalline.
 - No other intermetallic compounds are found in the NbAl_3 layer.

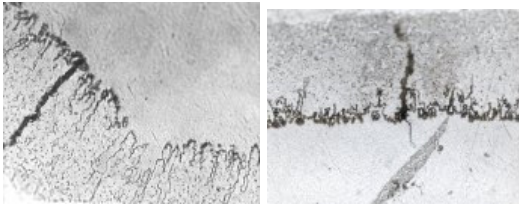


Figure 9a,b. Cracks in a dense NbAl_3 coating and crack running in the niobium.

The oxidation after cracking of the coating.

When a crack has been formed the niobium metal is oxidised.

The NbAl_3 -Nb boundary also oxidises because oxygen diffuses through the niobium to the NbAl_3 .

Even at a temperature of 605 °C NbO_2 needles are formed near the NbAl_3 (Figure 10a).

Farther from the NbAl_3 the needles change into the NbO-scale.

The NbAl_3 is lifted from the niobium metal, NbO_2 disappears while a thin NbO-scale is formed instead.

Finally the niobate will be deposited in the Nb_2O_5 phase at the NbO- Nb_2O_5 interface and the NbO-scale becomes, wider as shown in Figure 10b.

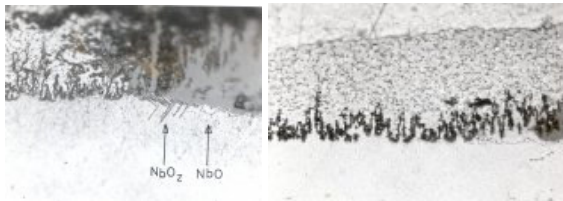


Figure 10a. NbO_2 needles are formed near the NbAl_3 . Figure 10b. The wide NbO-scale near the NbAl_3 .

DISCUSSION

Cracking

An explanation for the forming of cracks in the NbAl_3 is to be sought in the difference of the expansion coefficients of Nb and NbAl_3 .

It appeared that the cracks only occurred in a dense NbAl_3 layer which usually is not present before the oxidation. Thus, the formation takes place during the oxidation process, and it cracks as a result of the cooling because the expansion coefficient of NbAl_3 is greater than that of niobium. The mechanism of cracking is as follows. The crack starts within the dense NbAl_3 and is extended towards the niobium and to the free aluminium during cooling. When not much free aluminium is present the crack arrives at the surface and this enables oxidation of the niobium.

The formation of NbO_2

Figure 11 shows schematically the oxidation mechanism of the coating. Via breaks in the coating the niobium is oxidised and the oxygen diffuses through the niobium to the NbAl_3 -Nb interface. The NbAl_3 phase causes the oxygen to flow to NbAl_3 ; at the interface a niobate is formed. When the NbAl_3 has been oxidised the « sucking » effect decreases. It may be possible that the niobium at the NbAl_3 - Nb_2O_5 -Nb region becomes supersaturated with oxygen. It has been seen that NbO_2 can exist above 500 °C if niobium is oxidised in air. The supersaturating of niobium in the neighbourhood of the NbAl_3 could explain the existence of NbO_2 at a temperature such as 605 °C.

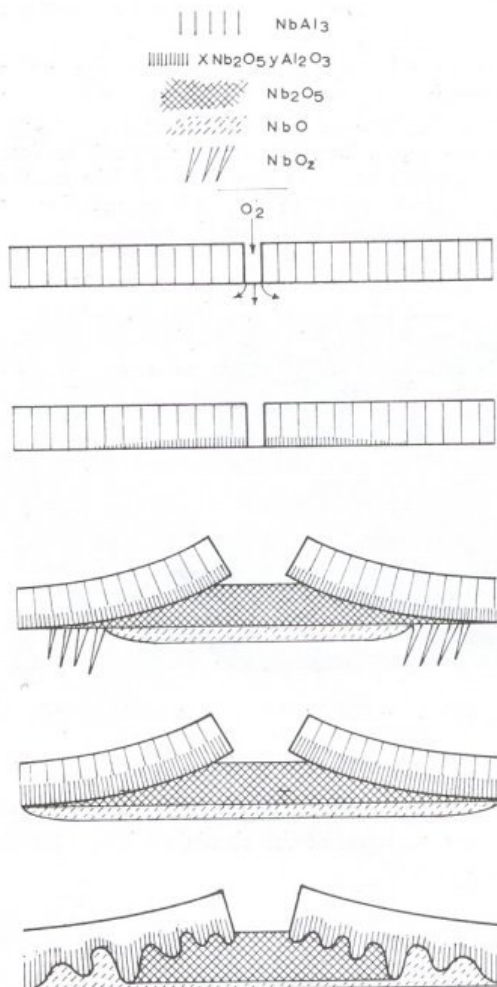


Figure 11. Oxidation mechanism of an Al coating on Nb.

The formation of the thick NbO-scale.

With longer oxidation times a thick NbO-scale is formed. The niobate formed at the Nb- Nb_2O_5 interface acts as a barrier for the diffusion of oxygen to the niobium.

Therefore the composition of the Nb_2O_5 will become more stoichiometric and the oxygen diffusion will decrease. In this case equilibrium is now attained and the NbO-scale will grow.

Oxidations in air at high temperature.

The dipped specimens were also tested in air at a temperature of 1100 °C. When the specimen had been well dipped coating remained intact for the relatively long time of 200 hours. When the specimen was cooled cracks occurred, and oxidation followed rapidly. During the oxidation a Nb_3Al and a Nb_2Al phase are formed (Figures 12a and 12b). Nb_3Al is a white compound between Nb and NbAl_3 whereas Nb_2Al is a strongly polarising network in NbAl_3 . It is not fully known why the coating ultimately fails after a considerable interval of time. The Nb_2Al network probably is responsible for it.

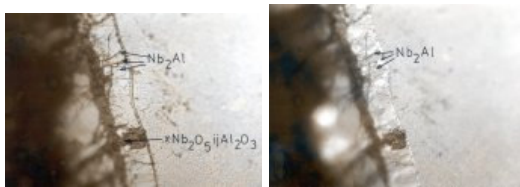


Figure 12a. Nb_2Al and Nb_3Al arise during oxidation at high temperatures. Non-polarising light.
Figure 12b. As Figure 12a, but with polarised light.

Efforts to improve the coating.

We have tried to improve the coating using a heattreatment.

The dipped specimens were heated in vacuum during one and four hours. During these heatings again a white non-polarising Nb_3Al region and the Nb_2Al network arise. Upon cooling the Nb_3Al layer cracks and these cracks also continue into the white region of Nb_3Al (Figure 13). The NbAl_3 layer is porous and the resistance to oxidation is poor, because cracks are present from the beginning of the oxidation.

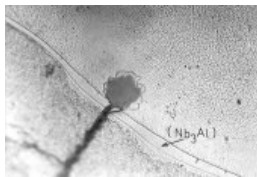


Figure 13. The crack in NbAl_3 runs into Nb_3Al and niobium oxidises.

CONCLUSION

The intermetallic compound NbAl_3 affords some protection against oxidation. At the interface Nb / NbAl_3 oxygen diffuses to the NbAl_3 giving a niobate which acts as a diffusion barrier.

However, when a crack is present NbO is formed which grows between niobium and niobate.

Cracks may arise by oxidation of free aluminium between NbAl_3 grains or by thermal stresses during cooling in a dense NbAl_3 diffusion layer.

REFERENCES

1. G.V. ESTULIN and N.N. BAROVA. The physics of metals and metallurgy. 12 (1961) 71.
2. N. NORMAN. J. Less Com. Met. 4 (1962) 52-61.

3. T. HURLEN. J. Inst. Met. 89 (1960) 273.
4. Th. L. KOLSKI. Trans. A.S.M. 55 (1962) 119-134.
5. R.A. MEUSSNER and B.F. BROWN. N.R.L. report 5550, July 1960.
6. R.G. CARLSON. Columbian Metallurgy (1960) 119.