

Study of Tantalum Powder Passivation upon Interaction with Nitrogen Gas

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Abstract – The work was aimed to investigate possible maximum reduction of oxide layer thickness and its replacement with a combination of Tantalum and Nitrogen to improve physical and electrical properties of powders. Upon the investigation it was found that during Nitrogen passivation powder specific surface area and starting passivation temperature are the most significant factors. Powders saturated with Nitrogen are less influenced by oxidation and in certain quantities show number of improved physical and electrical properties.

High development of microelectronics raised a need in designing more compact and power-intensive circuit diagram components and made stricter requirements for the materials used, in particular, Tantalum powders. It is known that the surface of Tantalum powder particle is covered with the oxide layer similar to Aluminum and other base metals. This layer thickness can reach 2 to 8 nm depending on the surface development [1, 2]. Characteristics of the oxide layer are rate and temperature of the oxidation reaction. The oxide layer is also a principal factor affecting final electrical properties of Tantalum capacitor powders. This paper discussed one of the existing opportunities of moderation (and partial suspension) of natural oxidation (forming the oxide film) and, consequently, upgrading the used properties of Tantalum powders.

The precondition of the study was instability of Tantalum powders upon interaction with the ambient air after undergoing operations reducing Oxygen, which was manifested in the non-verifiable oxidation of air with Oxygen and sorbitizing of contaminating impurities. An attempt was made to stabilize minimum thickness of the particle oxide film and prevent further oxidation by the passivation method. Among numerous alloying additives Nitrogen was a principal one, which in gaseous state had benefits in the use, introduction and achieving the preferable results not only in terms of chemistry but the technology too.

Prior to passivation the dissolved Oxygen was reduced to a maximum extent in the surface layer of Tantalum particle, where it was contained as oxides of TaO-Ta₂O₅ system. Thickness of that layer depended on powder specific surface area (SSA) and could vary depending on the conditions and methods of powder production. To remove oxide layers we used a method of Magnesium vapor reduction. The conditions of reduction were selected from references. Magnesium

was selected because of lower melting temperature (650 °C) and, correspondingly, higher partial pressure of vapor (compared with Ca and Al). Besides, complete acid washing to remove residual Magnesium and reaction products assisted in avoiding influence of the reductant remainder on further determination of the characteristics. We defined the reductant based on Oxygen contained in powder according to the gas assay and it amounted to 100–200% of the surplus quantity according to stoichiometry. De-oxidation of tantalum powder was conducted in a closed container made of Tantalum metal in a stream of Argon. In our case Argon was used both as a protective gas against oxidation and a carrier gas for Magnesium vapor. Prior to introduction into the equipment gas was subject to preliminary drying and cleaning. Temperature in the range of 800 °C to 1000 °C was selected so that to provide for as faster reaction as possible, on the one hand, and to avoid significant SSA reduction, increase of the average grain size, progress of the initial sintering stages and formation of strong agglomerates, on the other hand. Timing of the process, with some reserve, was limited by secondary indications of completing the reaction and amounted to 1.5 to 3 hours.

After de-oxidation we conducted passivation with Nitrogen gas considering that the particle surface was accessible for the reaction. Prior to introduction the compressed Nitrogen also underwent preliminary drying and cleaning.

Variable parameters during passivation were temperature inside the equipment upon introduction of Nitrogen, time of Nitrogen supply and its amount. The composition of the supplied gaseous atmosphere had only upper and lower limits of Nitrogen contained: "min" (1–2% in a mixture with Argon) and "max" (without dilution with Argon). To determine the significance of parameters we tested their affect on the powders of various genesis, which, presumably, had to affect the level of absorption of Nitrogen by the active surface and formation of the layer with different insusceptibility to oxidation. To enhance the effect of passivation depending on the parameter we tested different characteristics of the same type of powders.

The results of chemical assay of powders served as criteria to directly estimate the change of passivation parameters. Fig. 1 below demonstrated the results of Nitrogen accumulation per the time unit depending on passivation temperature. The initial powders contained slightly different Nitrogen, which was taken into account for calculations.

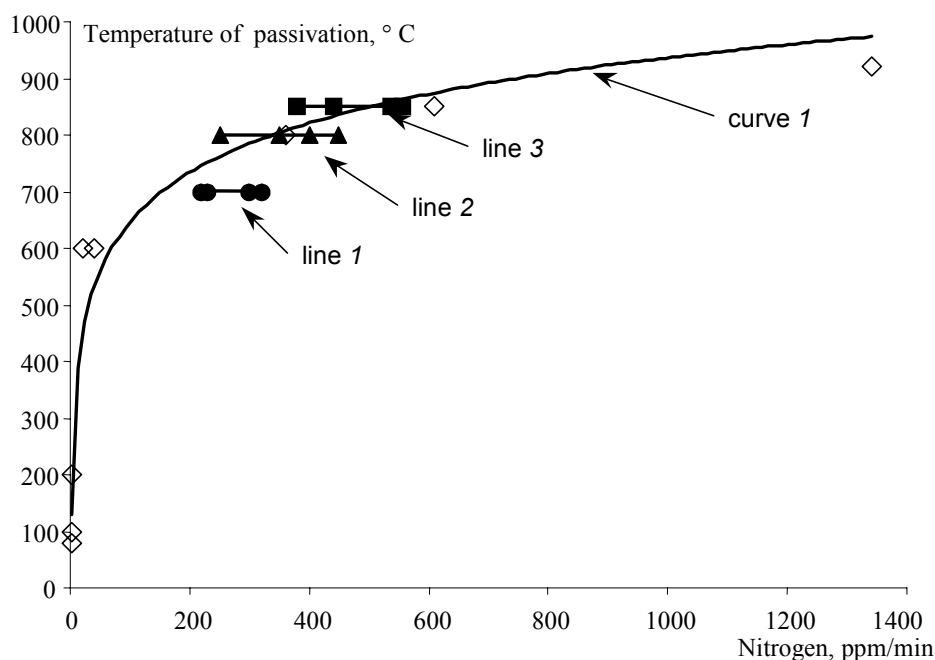


Fig. 1. Nitrogen accumulation rate as a function of temperature

Logarithmic curve 1 (Fig. 1), obtained by approximation of dots with higher reliability ($R^2 = 0.952$), demonstrated obviously the impetuous non-linear increase of the rate of Nitrogen accumulation at higher temperatures ($y = 126.14\text{Ln}(x) + 65.494$). Spread of dots in the range of the same temperature (Fig. 1: 700 °C – line 1, 800 °C – line 2 and 850 °C – line 3) demonstrated significant affect of powders structure with close values of the average grain size. Correlation analysis proved the interrelation between Nitrogen collected by powders and their average grain size. The best temperature area for passivation, which allowed obtaining stable results was within the range of 700÷850 °C.

Differences in Oxygen contained in the initial and passivated powders allowed to conclude about reduction of thickness of the particle surface oxide film partially due to passivation with Nitrogen gas. It is also confirmed by data about SSA and average grain size values, which remained unchanged. Besides, SEM study demonstrated identical structures of initial and passivated powders. The example of consistent structures of initial and treated powders is shown in Figs. 2–5.

To estimate potential substitution of the surface Oxygen for Nitrogen during passivation we selected powders with the developed SSA ($5\div 7 \text{ m}^2/\text{g}$) and, correspondingly, higher initial Oxygen ($1.4\div 1.7\%$). After de-oxidation conducted in a similar way, further passivation lasted for twice as longer time at temperatures of 700÷850 °C in a completely substituted atmosphere of the inert gas (Argon) for Nitrogen. Chemical assay showed close values of Nitrogen ($2.54\div 2.91\%$) and residual Oxygen ($0.16\div 0.18\%$). Reduction of Oxygen contained by ~10 times allowed to assume significant

reduction of the oxide film thickness and formation of a new protective system of N–Ta–O composition on the surface. Review of the changed composition of treated powders did not reveal any progress of oxidation upon interaction with the ambient air.

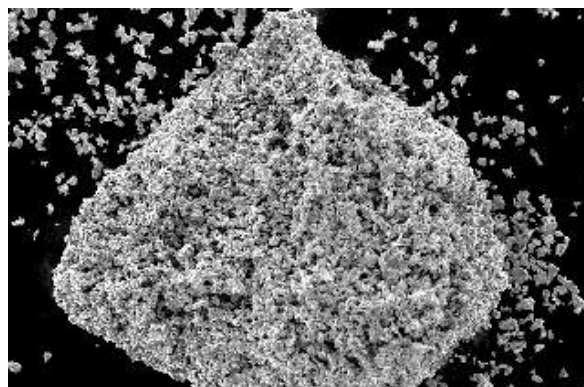


Fig. 2. Prior to treatment ($\times 250$)

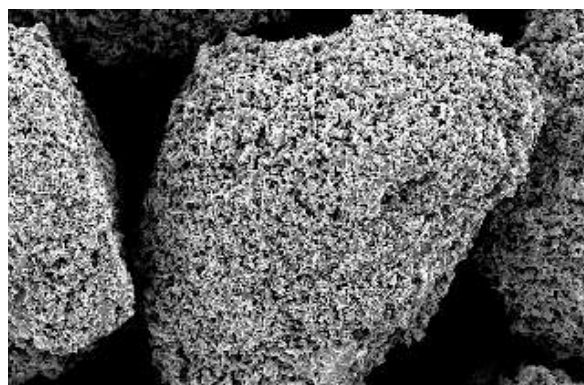
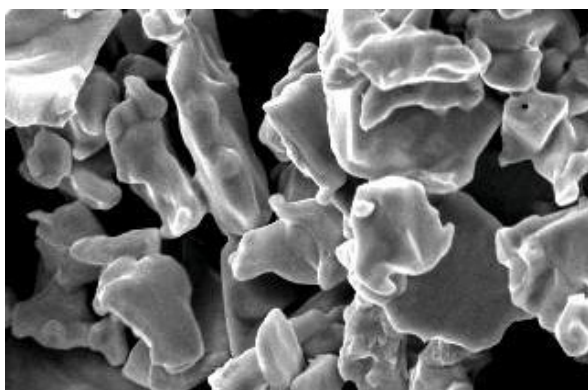
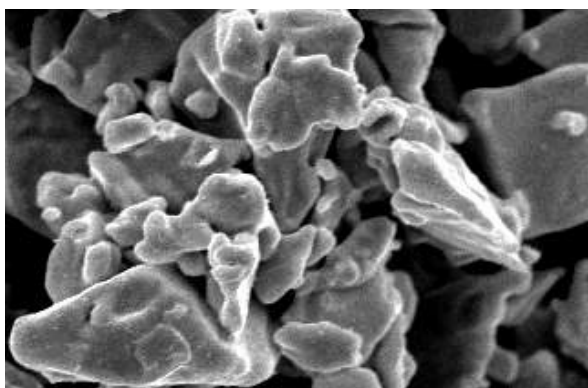


Fig. 3. After treatment ($\times 250$)

Fig. 4. Prior to treatment ($\times 250$)Fig. 5. After treatment ($\times 6000$)

To estimate potential substitution of the surface Oxygen for Nitrogen during passivation we selected powders with the developed SSA ($5\div 7 \text{ m}^2/\text{g}$) and, correspondingly, higher initial Oxygen ($1.4\div 1.7\%$). After de-oxidation conducted in a similar way, further passivation lasted for twice as longer time at temperatures of $700\div 850 \text{ }^\circ\text{C}$ in a completely substituted atmosphere of the inert gas (Argon) for Nitrogen. Chemical assay

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Influence of passivation with Nitrogen on physical and electrical properties of Tantalum powders was multipositional: in some powders Nitrogen contained at $0.15\div 0.25\%$ allowed to reduce leakage current, dissipation factor and shrinkage at insignificant reduction of specific charge; powders of another kind needed higher Nitrogen at $0.2\div 0.4\%$ to achieve the same results and the specific charge was reduced for $\sim 10\%$ in that case.

Conclusions: the studies of Tantalum powder passivation permitted to define the optimum passivation temperature range ($700\div 850 \text{ }^\circ\text{C}$), demonstrate a non-linear increase of the rate of Nitrogen accumulation at higher passivation temperature, reveal a possibility to significantly reduce Oxygen contained in the particle surface layer and simultaneously accumulate Nitrogen and determine multipositional influence of Nitrogen passivation on physical and electrical properties of powders.

References

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