The Eurasia Proceedings of Science, Technology,
Engineering & Mathematics (EPSTEM)
ISSN: 2602-3199

The Eurasia Proceedings of Science, Technology, Engineering & Mathematics (EPSTEM), 2024

Volume 28, Pages 477-483

ICBASET 2024: International Conference on Basic Sciences, Engineering and Technology

Oxidation of Sintered Refractory Alloy (Ni_3Al)

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Abstract: Ni_3Al is a superalloy which is of particular interest at high temperatures due to its high resistance to oxidation with the formation of a protective oxide layer that performs better than NiO and Cr_2O_3. Among the factors likely to affect the reaction mechanism and modification of the oxidation kinetics, the surface state appears to be a very important parameter. In the case of sintered materials, the surface condition will be linked to the porosity of the material and therefore to densification. This work essentially has two parts. The first consists of developing Ni_3Al sinters intended for oxidation, studying the densification mechanisms and bringing together the results obtained by dilatometry at variable temperature and by differential thermal analysis which made it possible to demonstrate sintering in a reactive liquid phase extremely fast SHS type, with instantaneous formation of the Ni_3Al phase. The second part is devoted to the isothermal oxidation between 1100 and 1350°C of cubic-shaped sinters (4mm edge) under a flow of oxygen for 24 hours. The shape of the parabolic curves is correlated with morphological and microstructural observations to deduce the diffusional kinetic regime which controls the speed of the reaction. On the other hand, these observations highlighted a very strong adhesion due to the indentations of the Al_2O_3 oxide in the metal at the oxide/metal interface. Various techniques (Density – XRD – SEM and Microanalysis) to characterize the sinters and the oxidation products complete our study.

Key words: Alloy, Ni_3Al, Sintering, Oxidation

Introduction

Nickel-based materials containing aluminum are used at high temperatures in aggressive environments (corrosion, irradiation, etc.). The choice of aluminum is motivated by the introduction of an element likely to lead to obtaining a refractory alloy. Aluminum is characterized by a high affinity for oxygen. However, it is practically unalterable in the air. This is due to the formation of a protective layer of alumina which has good corrosion resistance and constitutes a good electrical insulator. Various techniques have made it possible to develop the Ni_3Al phase by the SHS method (Mihelic, 1992), SRS (Thadani, 1992), reactive sintering (Bose, 1988; Hwang, 1992; Nashimura, 1993; Rabin, 1985), HIP (Chang, 1985), activation by grinding (Jang, 1991; Cardellini, 1994), or by infiltration (Dunand, 1994). However, certain authors such as (Bose, 1988 & Hwang, 1992), have developed the Ni_3Al alloy by natural sintering. The resistance to oxidation of alloys (Ni-Al) depends mainly on their composition (Rapp, 1984; Lacombe, 1984). Other scanning electron microscopy (SEM) and transmission microscopy (TEM) methods have been used to study the oxidation of Ni_3Al (Bobeth, 1992). It

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- Selection and peer-review under responsibility of the Organizing Committee of the Conference

appears from the bibliography that Ni_3Al has been widely studied in the bulk state, but little concerning sintered materials. So, it seemed interesting to us to study the influence of the microstructure and the addition of 13% by mass of aluminum on the oxidation of sintered nickel. According to the Ni-Al binary diagram (figure 1) (Singleton, 1986), the Al content of 13% predicts the Ni_3Al phase.

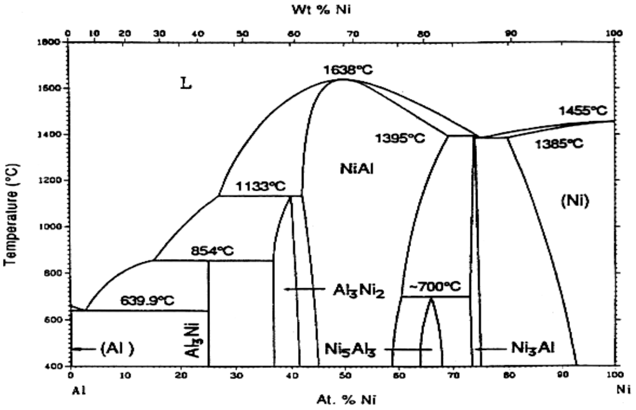

Figure 1. Ni-Al phase diagram.

Experimentation

The nickel and aluminum powders sold by Cerac have respective purities of 99.99% and 99.50%. Their respective average size is 5µm and 15µm. The powder mixtures (Ni-13% Al) by mass were carried out for 3 hours in a turbula. The agglomerates with a raw density of approximately 70% of the theoretical density were obtained by cold isostatic compression under 200 MPa for 2 minutes. The compacted bar obtained is cut into pellets (∅13mm and height 6mm) for the various heat treatments and characterizations. The shrinkage of the agglomerates was followed under dynamic argon U (3.5l/h) using a Setaram TMA92 type dilatometer at variable temperature, with heating and cooling rates of 5°C/min up to at 750°C. A differential thermal analysis (DTA) was carried out on the mixture up to 800°C under a flow of argon U (3.5l/h) at a rate of 10°C/min. The pellets were sintered under dynamic vacuum for 1 hour at a temperature of 750°C, with a heating and cooling rate equal to 20°C/min. Finally, various characterization techniques (XRD, Vickers density and microhardness measurements, and microstructural observations were implemented to characterize the sinters.

Isothermal oxidation was carried out on cubic samples (4mm edge) between 1100 and 1350°C, under oxygen flow for 24 hours, on polished surfaces up to 1µm. The evolution of the mass was monitored using a Setaram B85 thermobalance. The samples were characterized after oxidation by X-ray diffraction, scanning electron microscopy and microanalysis.

Results and Discussion

Sintering

The evolution of the linear shrinkage of the Ni-13%Al mixture presents a sudden shrinkage of amplitude of around 8%, manifests itself around 550°C, with an average expansion coefficient (between 20 and 550°C) of the order of $1.48.10^{-5}°C^{-1}$, calculated at cooling (figure 2). It is not preceded by any prior swelling and is followed by a regime of thermal expansion quite comparable to that which accompanies the initial heating stage. The densification curve is characteristic of liquid phase sintering. The shrinkage which occurs very suddenly is most certainly linked to the effect of this liquid phase which propagates at very high speed, leaving behind the solid compound Ni_3Al while causing the grains of Ni and Al to come together at the moment when they come into reaction. Undoubtedly linked to homogeneity problems, porosities can remain within the compound, as micrographic observation shows later.

The thermogram of the powder mixture (Ni-13%Al) by mass (figure 3) reveals the presence of a very energetic exothermic peak, reflecting the violence of the reaction corresponding to the stoichiometric composition of the Ni_3Al compound. However, preceding this reaction, we observe a small endothermic peak which could correspond to the formation of a molten aluminum phase but more probably to that of the eutectic liquid

(T=640°C). Indeed, some authors consider that the diffusion in the solid state of aluminum in nickel or in iron is already initiated even before its melting temperature is reached (Bose, 1988; Rabin, 1991; Gevanishvili, 2002), which seems to explain the sudden shrinkage at T=550°C on the shrinkage curve. It turns out that the formation of the liquid and the triggering of the reaction are almost concomitant.

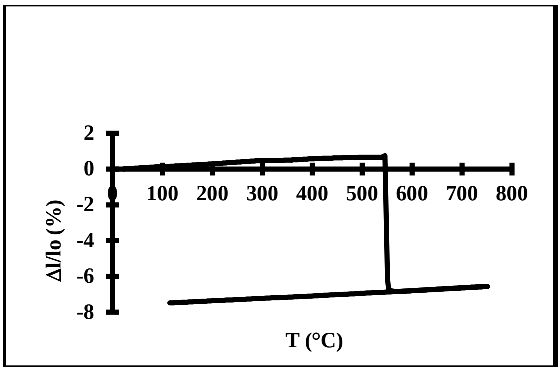

Figure 2. Dilatometry at variable temperature (Ni-13%Al) by mass.

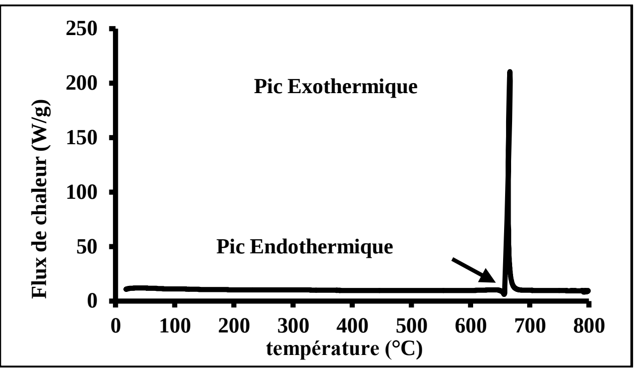

Figure 3. DTA curves of the mixture of the alloy (Ni-13%Al) by mass.

The diffractogram of the sintered alloy (Ni-13%Al) (figure 4) reveals only the single-phase compound Ni_3Al with a final density of 92% which would be consistent with the mechanism of reactive sintering described by (German, 1996). Morphological observations of the product formed (figure 5), after polishing and chemical attack, reveal the presence of pores and large grains of more or less rounded geometric shapes.

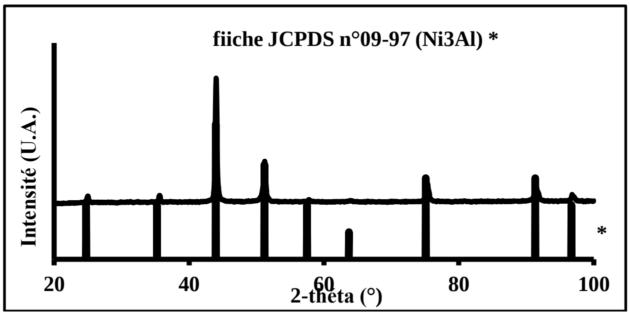

Figure 4. XRD spectrum of the sintered alloy (Ni-13%Al).

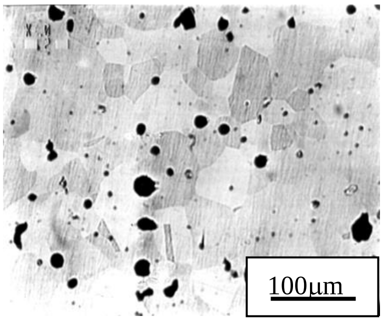

Figure 5. Microstructure of Ni_3Al

Oxidation

The isothermal changes in weight gain, per unit area and as a function of time, are shown in figure 6. These results show that the curves have a parabolic appearance whatever the oxidation temperatures between 1100 and 1350°C. They have low mass gain.

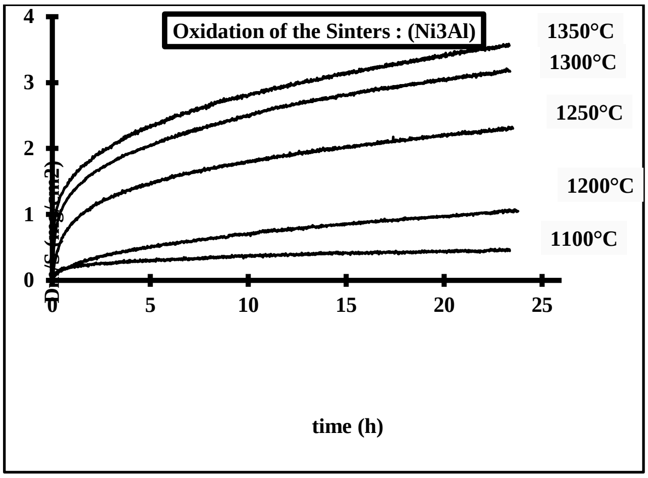

Figure 6. Mass gain per unit area of Ni_3Al.

From the oxidation temperature T=1200°C, X-ray diffraction analysis shows that the oxide formed on the surface of the sinters is alumina Al_2O_3. On the other hand, at T=1100°C, no oxide was revealed. Because at this temperature alumina is in an amorphous state and only crystallizes from1200°C (Castel, 1990). The oxide layer presents irregularities (non-uniform) which explains the presence of the two phases (Ni_3Al and Al_2O_3) by XRD (figure 7). To better exploit these results it is necessary to know the products formed by a morphological study on the surface and in cross sections as well as by microanalysis.

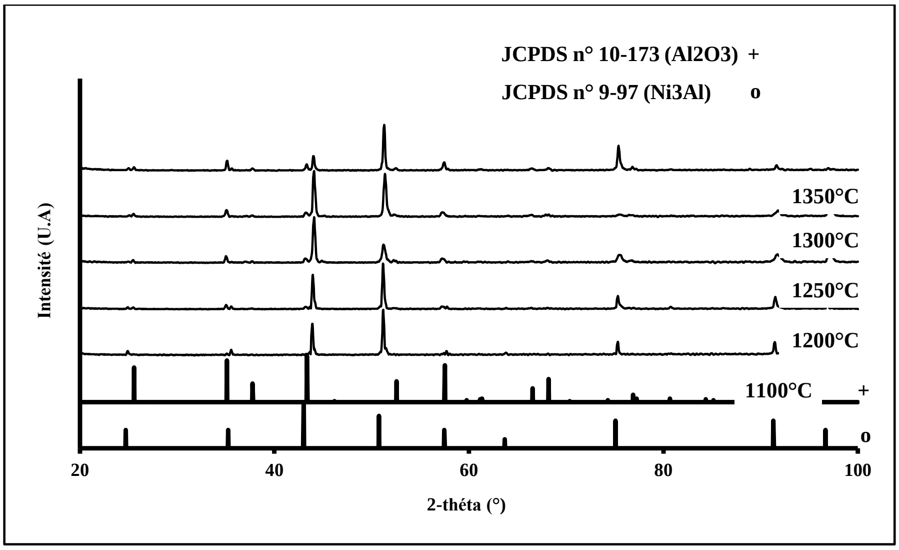

Figure 7. Diffractogram of Ni_3Al after 24 hours of oxidation.

The morphology of the oxidized frits changes very significantly with the oxidation temperature. The Ni_3Al sinter oxidized at T=1100°C (figure 8), shows the formation of two layers of oxide, one on the surface in the form of scales and the other underlying. They could be made of α-Al_2O_3 or $NiAl_2O_4$ spinel. But these compounds not having been identified by XRD, probably due to their low quantity and the limit of detection by X-rays, we have observed the oxide layer in cross section. Oxidation at T=1350°C seems to indicate a notable improvement from the recovery but porous point of view (figure 9).

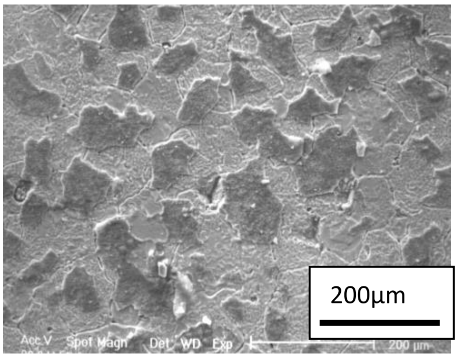

Figure 8. Scaled oxide (T=1200°C)

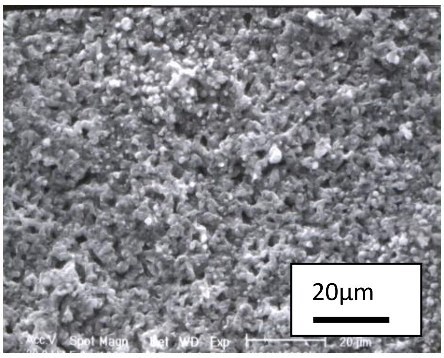

Figure 9. Porous Al_2O_3 (T=1200°C).

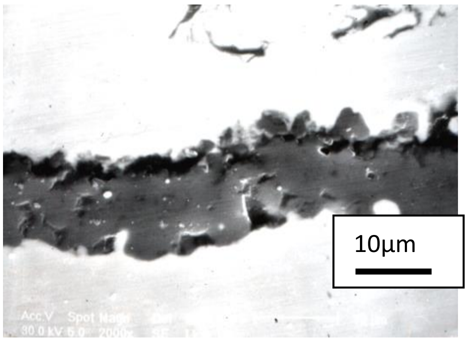

Figure 10. Oxide layer (T=1200°C).

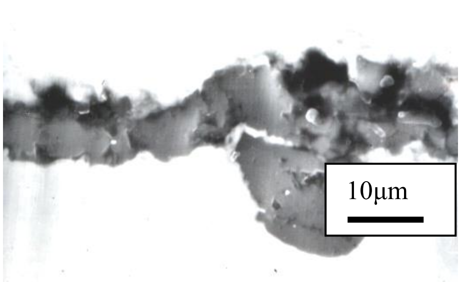

Figure 11. Oxide layer (T=1250°C).

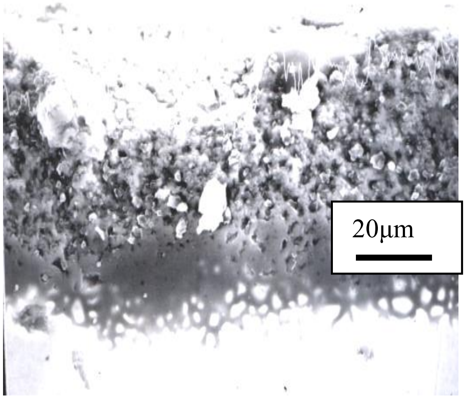

Figure 12. Oxide layer (T=1300°C).

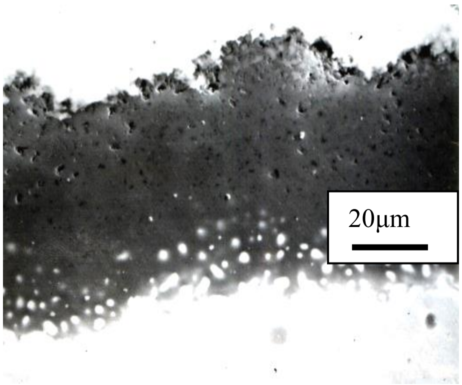

Figure 13. Oxide layer (T=1350°C).

The cross-sectional observation of the oxide layer at T=1100°C is very thin and cannot be detected by XRD, hence the difficulty in highlighting it in the cross section. On the other hand, on the other Ni_3Al sinters it highlights an internal growth of the oxide, 9at the grain boundaries of the metal. These inkings are the cause of good adhesion of the corrosion layer to the metal and confirm that the increase in temperature goes in the direction of an increase in the resistance to oxidation of the material (figures 10- 11-12-13). Overall, the oxide layer thickens with the percentage of aluminum, in accordance with the mass gain measured on the thermobalance.

By correlating the parabolic shape of the kinetic curves with microscopic observations, it seems logical to attribute the growth of the oxide layer to a diffusional process in the volume of Ni^{2+} which are mobile thanks to the nickel vacancies. The values of the rate constants kp deduced from the linear transforms at different temperatures (table 1) obey an Arrhenius law : $K_p = K_0.exp\left(-\frac{E_a}{RT}\right)$. The oxidation process is thermally activated with an energy of the order of $(160 \pm 10\frac{kJ}{mol})$ (figure 14). This value is lower than that of the nickel diffusion activation energy determined for single-crystalline NiO $\left(E_a \approx 247\frac{kJ}{mol}\right)$ (Atkinson, 1978). This difference can be attributed to the significant contribution of grain boundaries to the transport processes in the corrosion layer.

Table1. Rate constants of Ni_3Al oxidized.

Kp (mg.cm^2.s$^{-1/2}$)	0,065	0,2141	0,3295	0,4516	0,5259
T (°C)	1100	1200	1250	1300	1350

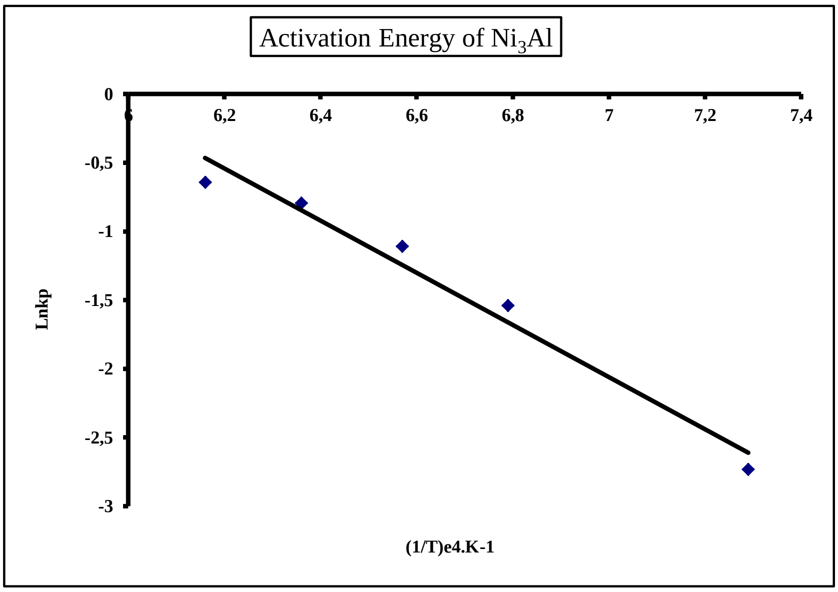

Figure 14. Arrhenius representation of the oxidation of Ni_3Al.

Conclusion

Ni_3Al sintering takes the form of liquid-reactive phase sintering, with a self-combustion type reaction, completely consuming both constituents. In this case, the transient liquid phase leads to the formation of the relatively dense intermetallic compound Ni_3Al. Regarding oxidation, given the low weight gain, Ni_3Al sinters have better resistance to oxidation. From 1200°C, there is the formation of an adherent and compact Al_2O_3 oxide layer in sufficient quantity which plays a protective role and is responsible for the best resistance to oxidation. The morphology of the oxide layer and the parabolic kinetics show that we are in the presence of a cationic diffusional process.

Scientific Ethics Declaration

The authors declare that the scientific ethical and legal responsibility of this article published in EPSTEM journal belongs to the authors.

Acknowledgements or Notes

* This article was presented as a poster presentation at the International Conference on Basic Sciences, Engineering and Technology (www.icbaset.net) held in Alanya/Turkey on May 02-05, 2024.

References

Atkinson, A., & Taylor, R.I. (1978). The self-diffusion of Ni in NiO and its relevance to the oxidation of Ni. *Journal of Materials Science, 13,*427-432.

Bobeth, M., Pompe, W., Schumann, E., & Ruhle, M., (1992). Out-diffusion of the noble component during the initial stage of the oxidation of γ'-Ni_3Al. *Acta Metallurgica Et Materialia, 40*(10), 2669-2676.

Bose, A., Rabin, B.H., & German R.M., (1988). Reactive sintering nickel-aluminide to near full density. *Powder Metallurgy International, 20*(3),25-30.

Cardellini, F., Mazzone, G., Montone, A., & Vittori-Antisari, M. (1994). Solid state reactions between Ni and Al powders induced by plastic deformation. *42*(7), 2445-2451.

Castel, B. (1990). *Les alumines et leurs applications* (p.54). Naathan.

Chang, K.M., Taub, A. J., & Huang, S.C. (1985). *High-temperature ordered intermetallic alloys* (Vol 38., p.335). *C*.C. Koch (Ed.). Pittsburgh, Pennsylvania: Cambridge University Press.

Dunand, D.C., (1994). NiAl formation by annealing of infiltrated aluminium-nickel precursors. *Journal of Materials Science,* (29), 4056-4060.

Gedevanishvili, S., & Deevi, S. C. (2002). Processing of iron aluminides by pressureless sintering through Fe+ Al elemental route. *Materials Science and Engineering : A, 325*(1-2), 163-176.

German, R.M. (1996). *Sintering theory and practice* (p.405). John Wiley & Sons.

Hwang, K.S., & Lu, Y.C. (1992). Reaction sintering of 0,1% B doped Ni_3Al, *Powder, Metallurgy International, 24*(5), 279-283.

Jang, J.S.C., & Koch, C.C. (1990). Amorphization and disordering of the Ni_3Al ordered intermetallic by mechanical milling. *Journal of Materials Research,5*(3), 498-510.

Lacombe, P., & Dabosi, F. (1984). Corrosion des matériaux à hautes temperatures, *Ecole d'hiver du CNRS Tome, 1,* 33-34.

Mihelic, B., Dahic, M., Djekic, R., & Uskokovic, D. (1992). Processing of compact materials by the use of self-propagating high-temperature synthesis and pseudo-hot isostatic pressing, *Materials Letters, 13, 391-395.*

Nishimura, C., & Liu, C.T. (1993). Reactive sintering of Ni_3Al under compression. *Acta Metallurgica Et Materialia, 1*(1), 113-120.

Rabin, B. H., &Wright, R.N. (1991). Synthesis of iron aluminides from elemental powders, Reaction mechanism and densification behaviour, *Metallurgical Transactions A, 22,* 277-286.

Rabin, B. H., Bose, A., & German, R.M. (1988). Processing effects on densification in reactive sintering of nickel-aluminum powder mixtures. *Modern Development in Powder Metallurgy, 20*, 511-529.

Rapp, R. A. (1984). The high temperature oxidation of metals forming cation-diffusion scales. *Metall. Trans. A, 15,* 765-782.

Singleton, M.F., Murray, J.L., & Nash, P. (1986). *Binary alloy phase diagrams* (Vol 1., p.140). T.H. Massalski, J.L. Murray, L.H. Bennett, H. Baker (Eds.). ASM, Metals Park.

Thadani, N.N., Work, S., Graham, R.A., & Hammetter, W. F. (1992). Shock-induced reaction synthesis (SRS) of nickel aluminides. *Journal of Materials Research, 7*(5), 1063-1075.

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To cite this article:

Halem, N., Halem, Z., Halem, O., & Petot-Ervas, G. (2024). Oxidation of sintered refractory alloy (Ni_3Al). *The Eurasia Proceedings of Science, Technology, Engineering & Mathematics (EPSTEM), 28,* 477-483.