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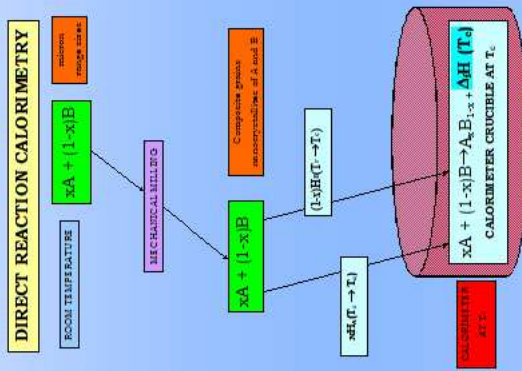
A new determination of the enthalpies of formation of tantalum carbides

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INTRODUCTION

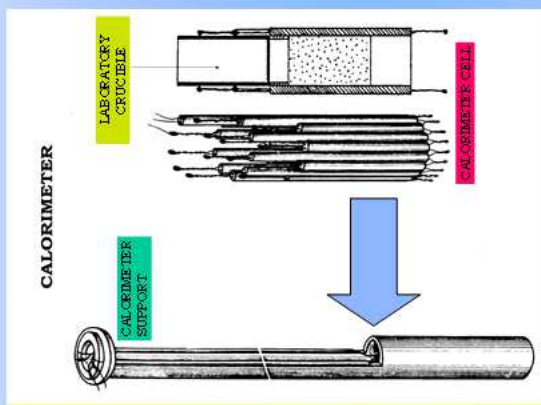
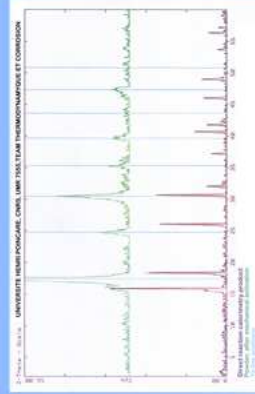
Among the hardening phases used to strengthen superalloys during their use at high temperature carbides may be very interesting, but their behaviour depends on the state of equilibrium of the alloy. In some cases carbides undergo drastic changes during high temperature service. The knowledge of the true equilibrium of the alloy is necessary to understand the carbides evolution. The CALPHAD method is a powerful tool to help in this procedure but the results depend on the quality of the experimental information used. This is the reason why we decided to check the values of the tantalum carbide enthalpies of formation by Direct Reaction Calorimetry. The problem is that reaction between tantalum and carbon leads to the formation of a superficial layer of carbide which blocks the diffusion. We had to use ball milling to get a composite powder of nanosized crystallites of Ta and C to obtain nearly complete reactions.



ENTHALPIES OF FORMATION (kJ/mole of atoms) MEASURED BY DIRECT REACTION CALORIMETRY.

Phase	Apparent heat result (kJ)	Literature	
		Lower limit	Higher limit
Ta _{1-x} C _x (Ta-C)	-33 500 (-1700)	-47 400 ⁽¹⁾	-63 100 ⁽²⁾
Ta _{1-x} C _x (TaC)	-34 500 (-1800)	-70 600 ⁽³⁾	-73 200 ⁽⁴⁾

(1) B.I. Smirnov and B.F. Gornat, *Dokl. Akad. Nauk. SSSR*, 100 (1955) 127.
 (2) O. Kubaschewski, V.I. Gerasimov, V.I. L'ubovitskiy, *Physico-Chemical Properties of 23 Compounds and Alloys*, Atomic Energy Series, International Atomic Energy Series, Vienna, 1972.
 (3) A.R. Korshak, I.D. Zakon, S.M. Skuratov, I.B. Dubovitskiy and G.F. Shvachin, *Russ. J. Phys. Chem.*, 41 (1967) 172.



CONCLUSION

This attempt to measure the enthalpies of formation of refractory phases by direct reaction calorimetry shows that there exists a possibility to obtain results even if the calorimeter temperature is too low to ensure a complete and quick reaction (even at 1800K) with classical micron sized powders. Obviously our enthalpy results show that a part of the heat of reaction is still missing, but this fact may be explained by the X-ray pattern of the as-milled powder. There is already a detectable quantity of TaC. This shows that the activation was not correct. To get definitive results, the milling has to be optimised and this part of the work may not be easy. But, on the other hand increasing the calorimeter temperature up to 2000 K or more would certainly be by far more difficult and damaging for the measurement accuracy.