SUMMARY

Oxidation resistant alloys undergo very rapid, often catastrophic degradation in sulphur containing atmospheres. In spite of this, however, the mechanism of sulphide corrosion of metallic materials is still less known than in the case of oxidation. Such a situation results mainly from much greater experimental difficulties in studying the high temperature reactions in sulphur containing atmospheres. Sulphur vapours are, namely, extremely aggressive at high temperatures and as a consequence, all standard thermogravimetric and other equipments commonly used in oxidation studies are not applicable under such conditions. This important experimental restriction has been overcame in the presented work by the development of novel microthermogravimetric assembly, enabling the determination of the kinetics of mass changes of a given sample with the accuracy of about two orders of magnitude higher than in all other thermogravimetric equipments, i.e. of the order of 10^{-7} g. In addition to precise measurements of sulphidation kinetics, this apparatus makes it possible to study the concentration and the mobility of point defects in metal sulphides showing not only large, but also very low deviation from stoichiometry. Thus, the experimental basis has been created to obtain novel information on transport properties of a number of metal sulphides (MnS, NbS_2, NiS, Co_4S_3, Co_9S_8) participating in scales formed on high temperature alloys in composed industrial atmospheres. The concentrations of predominant defects in these sulphides have been obtained from nonstoichiometry data and the mobility of these defects was determined using re-eqilibration and two-stage kinetic methods. In order to get direct correlation between these information with the kinetics and mechanism of corrosion, all experiments have been carried out on scales obtained by complete sulphidation of a given metal, i.e. on samples with definite texture.

One of the most important results obtained in the present work constitutes the data describing the mobility of predominant defects in niobium disulphide being the main product of niobium sulphidation. It has been shown, namely, that the mobility of these defects is several order of magnitude lower than those in all other so far studied metal sulphides and oxides. These results made it possible to explain the main reason of very high resistance of niobium to sulphide corrosion in spite of high defect concentration in NbS_2 phase. On the other hand, it has been demonstrated, that if the defect concentration in the sulphide scale of a given metal is rather low, like in the case of manganese sulphidation, protective properties of the scale may highly be improved by doping effect.