different Cr/Mn ratios vs. temperature and original steel compositions $(Cr, Mn)_2O_3$ had very little manganese, so it was not considered for further analysis). In order to find this correlation, spinel compositions of these ferritic steels were located onto the Mn_2O_3 - Cr_2O_3 phase diagram, shown in Figure 6 (Golikov *et al.*, 1987).

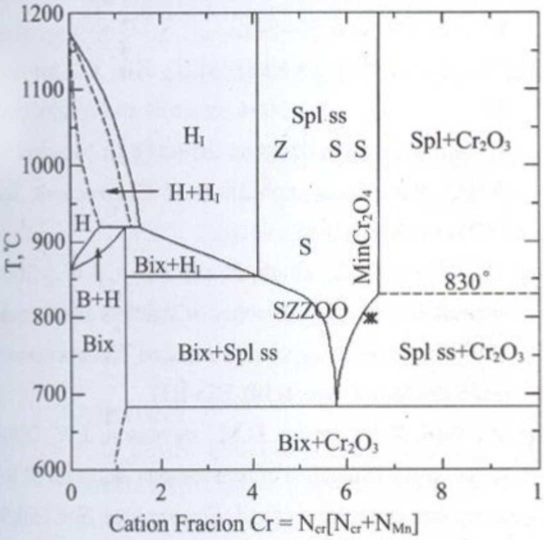

Fig. 6. Phase diagram of Mn_2O_3 - Cr_2O_3 by (Golikov *et al.*, 1987) with experimental points of the present study (X – 430, O – ITM14, S – Crofer22APU, Z – ZMG232).

All theses steels have spinel formation at 800°C with composition varied by increasing Mn fraction in order Crofer > ZMG > ITM > 430. Steels AISI 430 and ITM14 ceased to form distinct spinels at 900-1000°C, whereas Crofer has the most steady spinel composition (Cr/Mn = 1…1.5). ZMG232 produces nearly stoichiometric spinels at 900°C (Cr/Mn ~2) but one with composition more close to hausmanite at 1000°C (Fig. 6). It is not clear, whether this is caused by a higher Mn content in ZMG vs. other equivalent steels or by impact of minor alloying elements (even higher Mn content in AISI 430 does not count due low chromium content in this steel). Except for small titanium contents, no active elements (La, Zr, Y) were found in oxides or in spinels during EDX analysis of surface scale at all cases.

During oxidation a depletion of the scale forming elements, mainly Cr, leads to a change in the composition of the surface scale and consequently also to a change in the oxide growth rate. Lower initial concentration of chromium in the alloy (< 20%) leads to a slight increase of the oxidation rate. Not only depletion of chromium, but also manganese is responsible for this oxidation behaviour. Manganese is known to play an important role in the oxidation mechanism of the ferritic steels and, due to its low concentration, it will exhibit completely different depletion kinetics as chromium (Huczkowski *et al.*, 2004). Although Cr/Mn ratio in spinels does not explicitly correlate with oxidation temperature neither equivalent chromium content, it seems that "good" spinel formers for initial stages of oxidation are ferritic steels with ECr ~21… 24, low titanium and increased manganese.

4. Conclusion

The oxidation behaviour of ferritic stainless steels has been studied in the temperature range 800-1000°C in static air for 24-168 hours. A significant difference in oxidation process between studied steels has been observed. Mass changes were ~40 mg/cm^2 AISI 430 and ±1.5 mg/cm^2 for all others steels.

Surface observation of the air oxidized specimens by SEM show the differences in oxide layer formation. Chromia- and spinel-rich layers (as well as single crystallites) were observed for all steels at 800°C. At higher temperatures (900 and 1000°C) the growth of spinel with different composition was found for ZMG232 and Croffer22APU only. Alloys AISI 430 and ITM14 showed at these temperatures only oxides like Me_2O_3. The effect of active element additions (La, Zr, Y) was not directly observed in this study neither they were found in oxides or in spinels. "Good" spinel formers for initial stages of oxidation are ferritic steels with ECr ~21…24, low titanium and increased manganese, whereas processing for thermally grown spinel is likely better to carry out at elevated temperatures (over 900°C) but with shorter times.

5. Acknowledgments

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References

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