The Corrosion Behaviour of Refractory Metals against Molten and Evaporated Zinc

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Abstract

It is well known that refractory metals like molybdenum, tungsten and their alloys show reasonable to excellent corrosion resistance against molten zinc at temperatures up to about 500℃. There are also indications that especially molybdenum is again corrosion resistant at high temperatures of around 800℃ above a temperature zone of higher attack in between. Presumably this behaviour is caused by the thermodynamics and kinetics of the formation or retention of Zn-Mo intermetallic phases. In this work the corrosion behaviour of refractory metals / alloys against Zn melt and vapour in the intermediate temperature range of 500 to 700℃ is investigated m ore intensely. It can be shown that molybdenum can probably be used more frequently in this temperatur range than has been thought up to now.

Keywords

Corrosion, molybdenum, tungsten, alloys, steel, grafite, molten zinc, dissolution, vapor

Introduction

In steel industry various techniques of the application of zinc coatings are used. All of them – immersion in molten zinc or in zinc vapor – need materials which are fairly resistant against zinc. There are a few publications treating this item [1,2], but nevertheless it seems that there is no complete solution existing so far. Therefore in this work the refractory metals/alloy Mo, W and Mo-30wt%W have been investigated and have been compared to a heat resistant steel H525 (DIN 1.4841) and to grafite concerning zinc corrosion resistance in the temperature range 500 to 700℃.

Experimental

For preparation the samples of the materials were immersed in molten zinc at 480℃ and then – in case of T = 500℃ – exposed to nitrogen (quality 5.0) fo r 168 hours. A pretest at 700℃ did not give reasonable results, as the zinc was evaporated quickly and was deposited outside the testing zone by resublimation in colder regions of the furnace. Therefore the filled crucibles were put into tubes of borosilicate glass, evacuated, sealed (by melting; fig. 1) and were tested subsequently at 600, 650 an 700℃ in an air furnace again for one week.

Fig. 1: Macro of borosilicate tubes with samples inside after testing

The materials samples to be tested were machined from rods or sheet prematerial, cleaned in an aqueous detergent with ultrasonic excitation and dried. After the tests half of the samples were submitted to cross sectioning, from the second half the zinc was removed by etching with diluted hydrochloric acid for gravimetric evaluation.

Results and Discussion

Table 1 shows the gravimetric changes of the materials which were tested. Molybdenum looses mass at 500℃ and gains mass from 600 to 700℃ with decreas ing tendency. This can be explained by the formation of a Mo-Zn-intermetallic phase at the lowest temperature with decreasing thermodynamic stability up to 700℃ (see Mo-Zn-phase diagramm, fig. 6). At 700℃ no formation of an intermetallic phase can be expected which leads to a comparably low corrosion rate at the highest temperature that was applied.

Table 1: Specific mass changes in mg/(cm^2) after 168 hours testing in molten Zinc at various temperartures

Temperature (℃)	500	600	650	700
Material				
Mo	-98,49	15,27	14,60	1,69
Mo-30W	-0,75	-0,27	-0,40	-0,29
W	0,00	-1,17	-0,22	-0,03
H525	dissolved	dissolved	dissolved	dissolved
Grafite	no result	burned (access of air)	0,05; -0,17	0,50

This phase seems to be fairly soluble in diluted hydrochloric acid (mass loss; fig. 2). The mass gains can be explained by the formation of different phases. The corrosion depth can be seen in table 2.

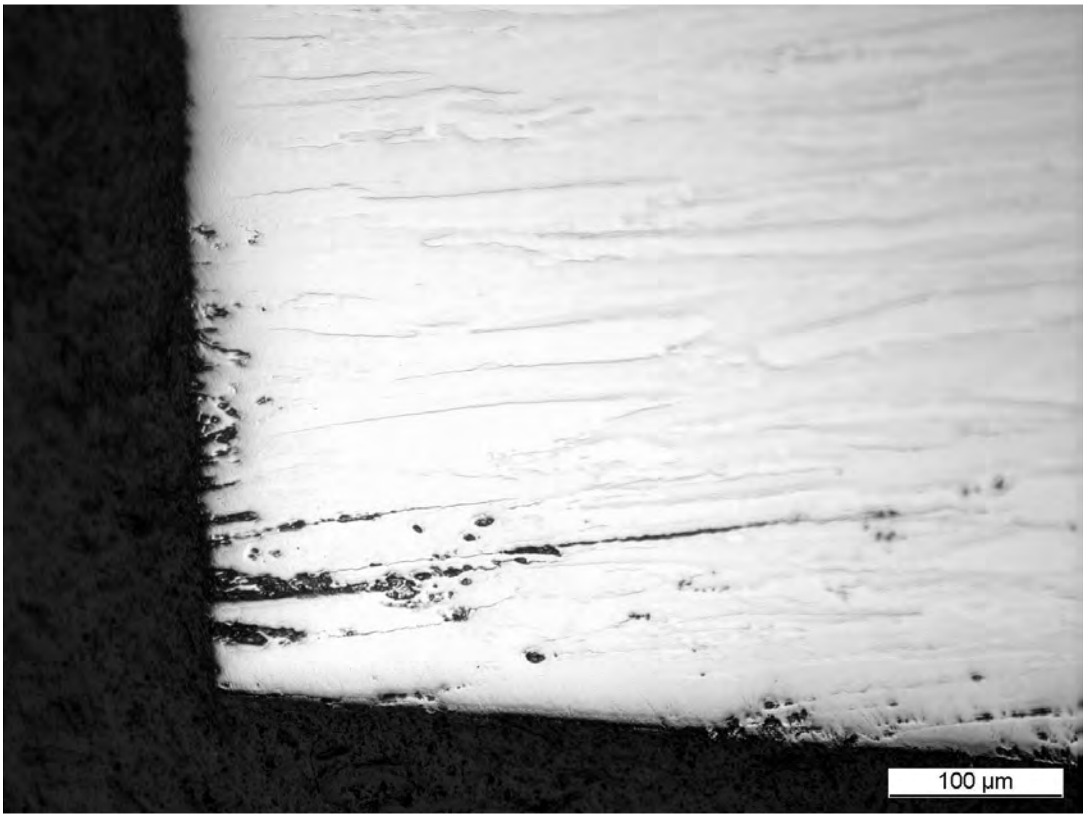

Fig. 2: Optical light micrograph of a cross section of Mo after 168 h in molten Zn at 500℃ (HCl etched)

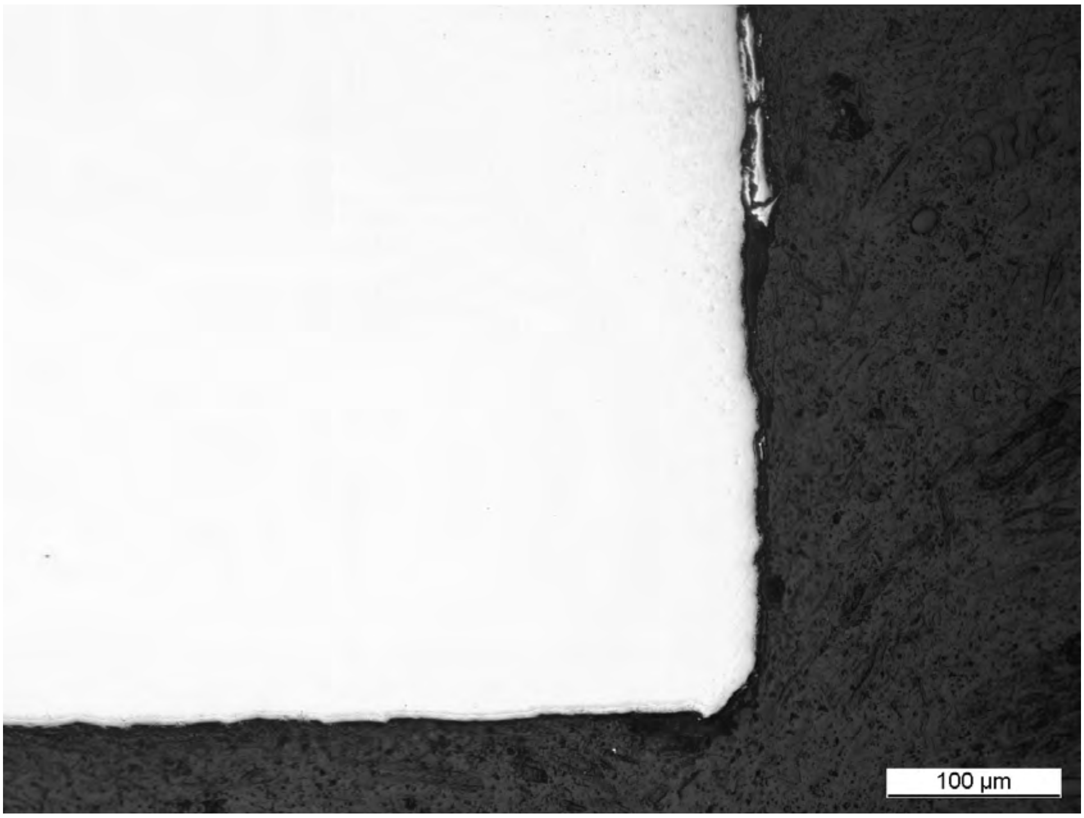

Fig. 3: Optical light micrograph of a cross section of W after 168 h in molten Zn at 500℃ (HCl etched)

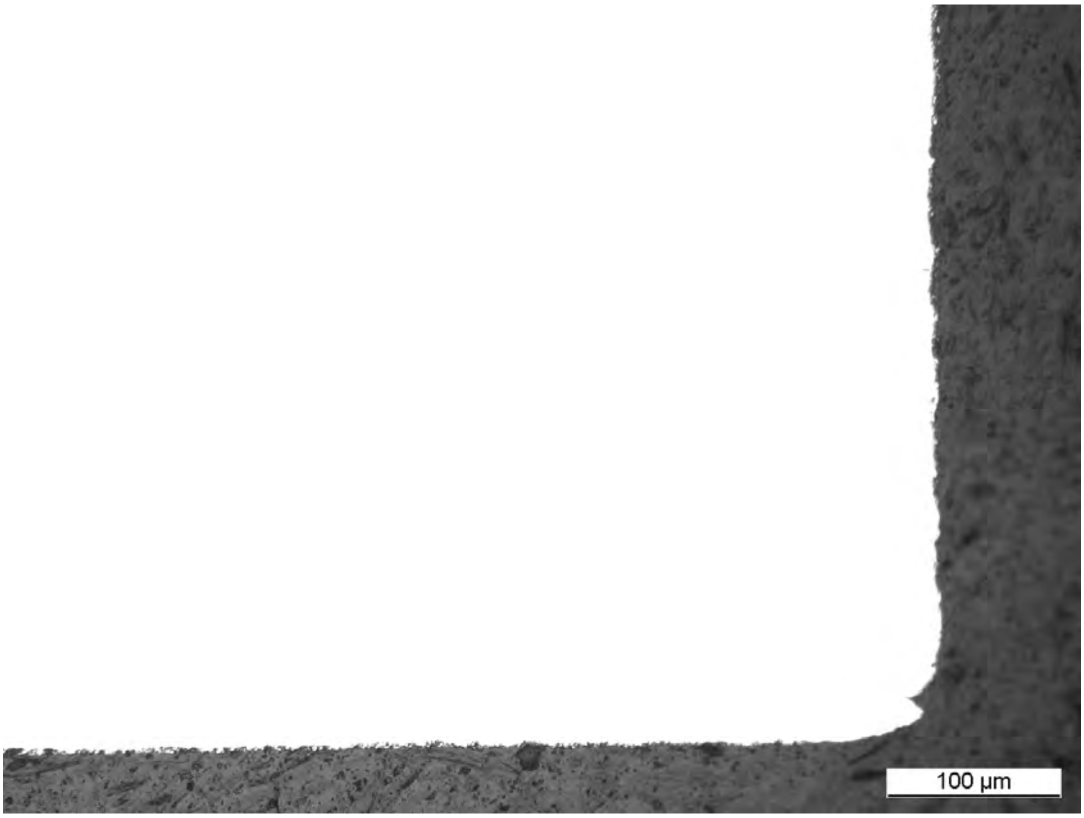

Fig. 4: Optical light micrograph of a cross section of MoW after 168 h in molten Zn at 500℃ (HCl etched)

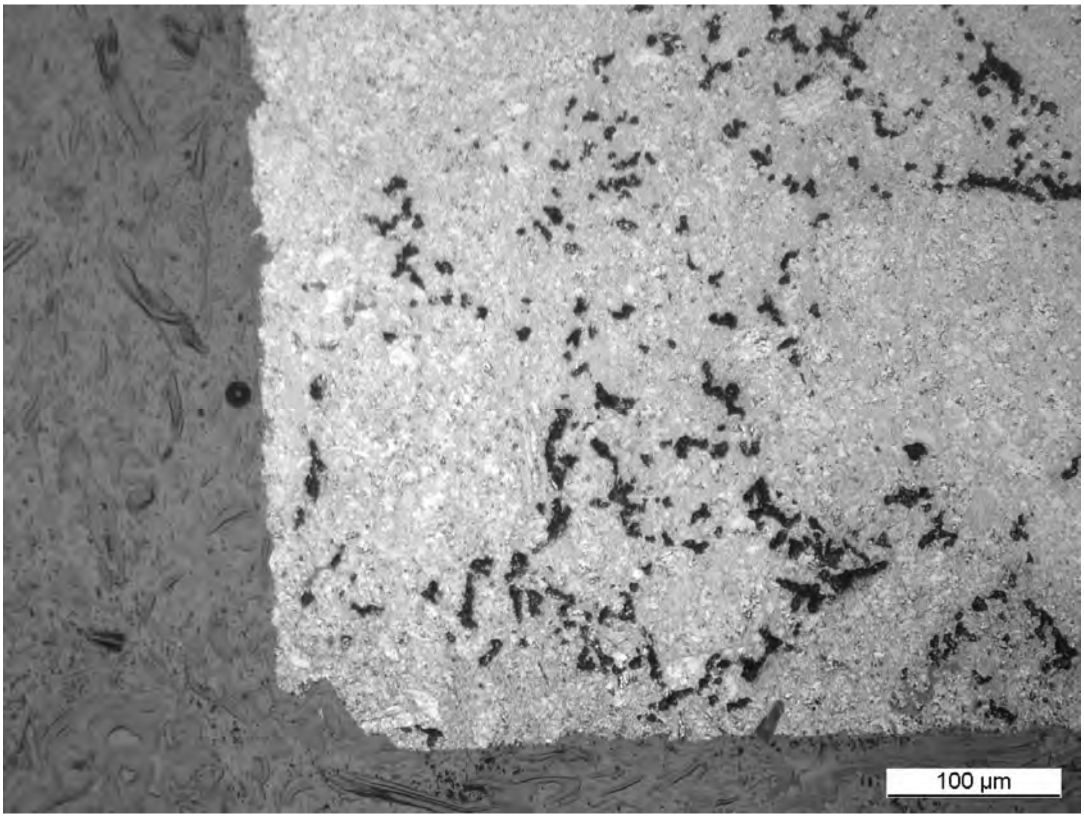

Fig. 5: Optical light micrograph of a cross section of grafite after 168 h in molten Zn at 650℃ (HCl etched)

The masses of the samples of Mo-30W, W and grafite are slightly changed in general (table 1) however at 700℃ grafite exhibits a significant mass gain w hich may be caused by some penetration of zinc melt into the porous structure (see also fig. 5). In case of W and Mo-30W the low mass change is confirmed by the very low corrosion depths which were determined from the corresponding cross sections (table 2). The ASM phase diagram data base does not contain W-Zn and C-Zn phase diagrams but citations which mention a weak interaction of W and C with Zn. Also the optical light micrographs of figs. 2 to 5 do not indicate a remarkable corrosion attack; only a slight roughening of the surface can be detected. The heat resistant steel is dissolved by the zinc melt at all temperatures which were applied. This can be explained by the corresponding phase diagram Fe-Zn (fig. 7): Above 500℃ there is high solubility of iron in the molten zinc.

In table 3 extrapolated corrosion rates are shown: the first value assuming a parabolic mechanism, the second value from a linear rate law. In case of Mo the values are based on maximum corrosion depths (after HCl etching), in case of the others mass losses after HCl etching have been used for calculations. It can be seen that molybdenum is strongly attacked at 500℃ and significantly less at 650℃. At 600℃ and at 700℃ it is more resistant. This is most pro bably caused by the changing phase stabilities and solubilities of the Mo – Zn system in the selected temperature range.

Table 2: Corrosion depth in µm after 168 hours testing in molten Zinc at various temperartures

Temp. (°C)	500	600	650	700
Material				
Mo	1000 - 1500*	100 - 150 *	300 - 650 *	100 - 300 *
Mo-30W	0,00	0,00	0 **	0 **
W	0,00	0 ***	0 **	0 ****
H525	>= 9000*****	>= 9000*****	>= 9000*****	>= 9000*****
Grafite	no result	burned (access of air)	0,00	0,00

* value dependent on grain versus surface orientation (transversal: higher)
description of the attack: porosity after HCl-etching

** small porosity close to the surface

*** small bulk porosity

**** small roughening of the surface with transversally cut grains

***** sample completely dissolved

Assessed Mo-Zn phase diagram.

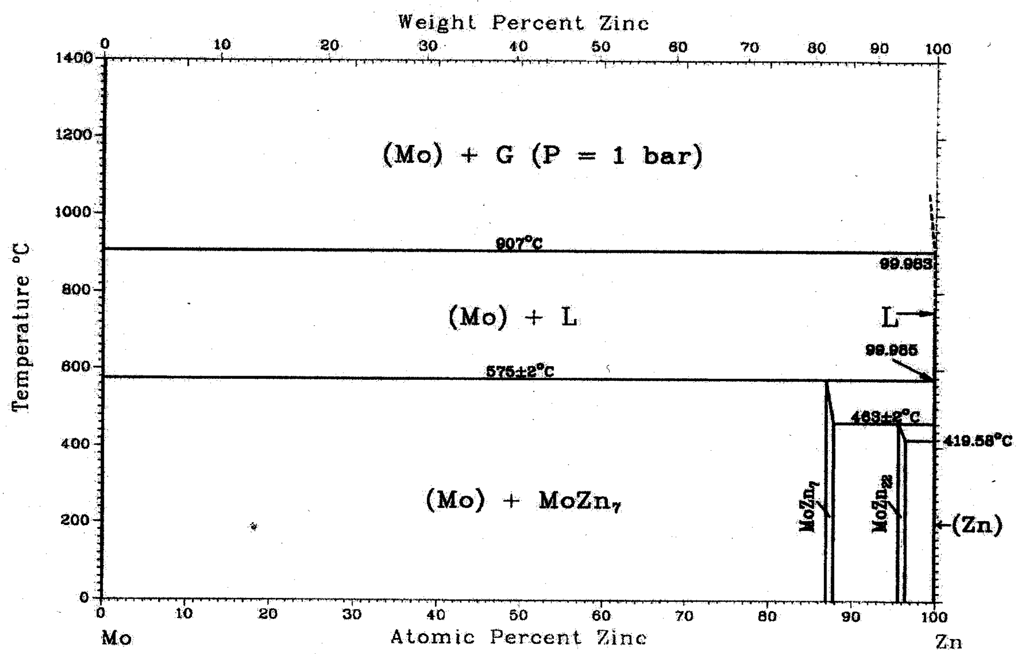

Fig. 6: Mo – Zn – phase diagramm (ASM)

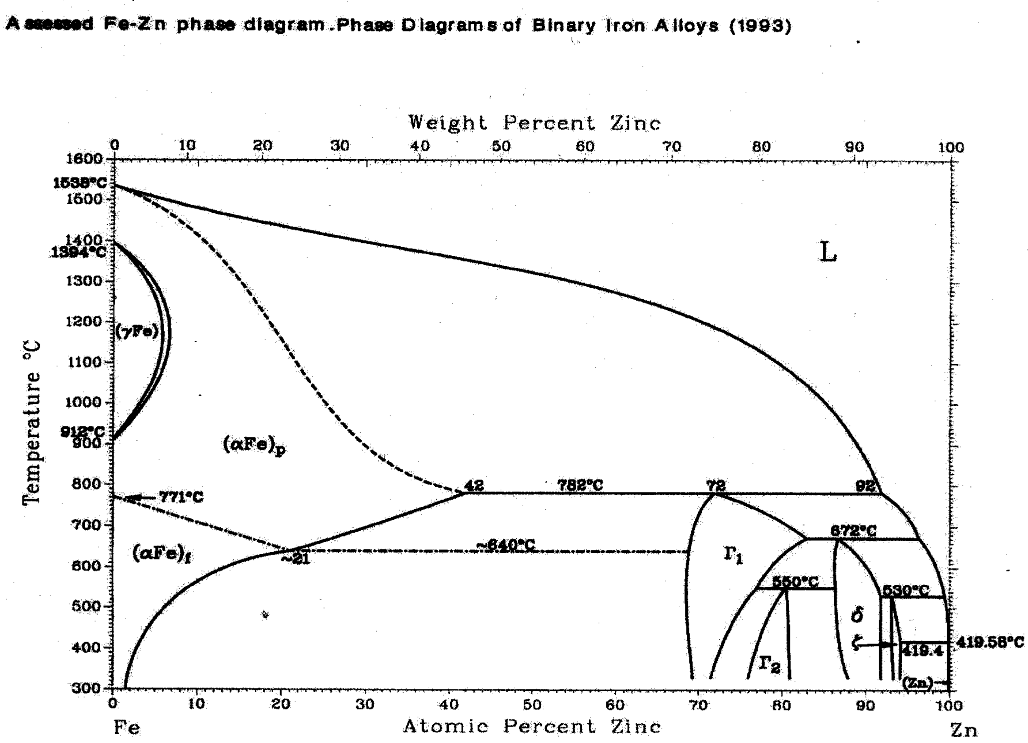

Fig. 7: Fe – Zn – phase diagramm (ASM)

Table 3: Extrapolated maximum parabolic and linear corrosion rates (R(p); R(l)) in mm/year at various temperatures

Temp. (℃)	500	600	650	700
Material				
Mo *	7 ; 52	1 ; 8	5 ; 34	2 ; 16
Mo-30W **	0.004 ; 0.03	0.001 ; 0.01	0.002 ; 0.01	0.001 ; 0.01
W **	0	0.004 ; 0.03	0.001 ; 0.01	0
H525	***	***	***	***
Grafite	no result	burned (access of air)	appr. 0	appr. 0

* Calculated from maximum corrosion depth (cross section) after HCl-etching

** Calculated from mass losses of samples with HCl-etching

*** Sample dissolved

Preliminary tests of Mo, Mo-30W and W against zinc vapour at 700℃ showed only a slight surface attack preferentially at the grain boundaries.

Conclusions and Outlook

Molybdenum, Mo-30W, tungsten, steel H525 and grafite have been exposed to molten Zn at 500, 600, 650 and 700℃ for 168 hours. The heat resistant ste el was dissolved, molybdenum showed corrosion effects mainly at 500℃ and 650℃, whereas Mo-30W, W and grafite revealed to be more or less resistant. The explanations can be given using the phase diagrams or other informations of the ASM – data base. Because of its porosity and lower strength the grafite is no serious competitive material for the refractory metals/alloy. When temperatures can be kept above 600℃ and corrosion rates of up to 35 mm / year are acceptable molybdenum can be used with its benefits for more complicated parts. First experiments with Zn vapour at 700℃ indicate minor corrosion attacks than with molten zinc. This has to be confirmed by additional tests and investigations.

References

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