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# Effect of manganese on the cavitation erosion resistance of iron–chromium–carbon–silicon alloys for replacing cobalt-base Stellite

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## Abstract

The cavitation erosion behavior of Fe–Cr–C–Si–$x$Mn ($x = 5$, 10 and 15 wt%) alloys were investigated for 50 h using 20 kHz vibratory cavitation erosion test equipment. Low-Mn alloys (<5 wt% Mn) and high alloys (>10 wt% Mn) exhibited the $\gamma \rightarrow \alpha'$ and $\gamma \rightarrow \varepsilon$ strain-induced martensitic transformation, respectively. Mn-addition above 10 wt% was observed to increase the cavitation erosion resistance of the Fe-based alloy. It was concluded that the $\gamma \rightarrow \varepsilon$ strain-induced martensitic transformation would be more beneficial than the $\gamma \rightarrow \alpha'$ strain-induced martensitic transformation due to the blocking of the dislocation motion, thus increasing the hardness of the matrix by effective work-hardening. The phase transformation was examined by X-ray diffraction before and after the cavitation erosion tests and the surface damage of the tested specimens was also investigated by scanning electron and optical microscopy.

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## 1. Introduction

Co-based Stellite alloys have traditionally been used as hardfacing materials for nuclear power plant valves due to their superior cavitation erosion resistance as well as sliding wear resistance [1]. However, Co is known to be one of the main contributors to the occupational radiation exposure [2]. Thus, for safety concerns, it is desirable to replace the Stellite 6 with cobalt-free hardfacing alloys having the equivalent properties. High corrosion resistance, cavitation erosion resistance and wear resistance are generally required for hardfacing materials in nuclear power plants. Cavitation erosion is caused by a gas cavity or bubble formation and sudden burst. The repeated collapse of these cavities can cause severe damage on metal surfaces [1,2].

According to Ohriner et al. [3], the cavitation erosion resistance of the Fe-based alloys is higher due to work hardening and they attributed the observed enhancement to the strain-induced ε martensite phase transformation. Nevertheless, although many erosion resistant alloys do undergo phase transformations, no simple correlation has been established between the phase transformation

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and cavitation erosion resistance. It has been suggested that the formation of martensite leads to a high work-hardening rate and the subsequent high ultimate stress levels while maintaining good uniform elongation [4]. These two properties are important in withstanding the cavitation erosion. It was also reported that the addition of Mn could improve the cavitation erosion resistance of the Fe-based alloys due to the formation of ε martensite composed of twins and tangled dislocations. The present study is an attempt to evaluate the cavitation erosion resistant hardfacing alloys such as Fe–Cr–C–Si–$x$Mn ($x = 5$, 10 and 15 wt%) alloys and Stellite 6 up to 50 h using 20 kHz vibratory cavitation erosion tester.

## 2. Experimental procedure

Cast ingots of Mn added Fe-based alloy and Stellite 6 were used. The chemical compositions of the alloys are shown in Table 1. Cavitation erosion tests were performed using a vibratory cavitation erosion-testing machine in accordance with ASTM-G32 [5]. A schematic diagram of the apparatus is shown in Fig. 1. The apparatus used a commercial ultrasonic oscillator supplied by Hanyang Ultrasonic Co., Ltd.

## 3. Results and discussion

The cumulative weight losses of Fe–Cr–C–Si–$x$Mn ($x = 5$, 10 and 15 wt%) alloys and Stellite 6 were measured during cavitation erosion test every 2 h for a period of 15 h and then every 5 h for a period of 50 h. The results are presented as a function of the exposure time in Fig. 2. The incubation times for 5, 10 and 15 wt% Mn and Stellite 6 were measured to be 5, 8, 8 and 6 h, respectively. These values are longer than or similar to that of the Stellite 6. The incubation time during the early stage of cavitation erosion could be related to the plastic deformation behavior of the material.

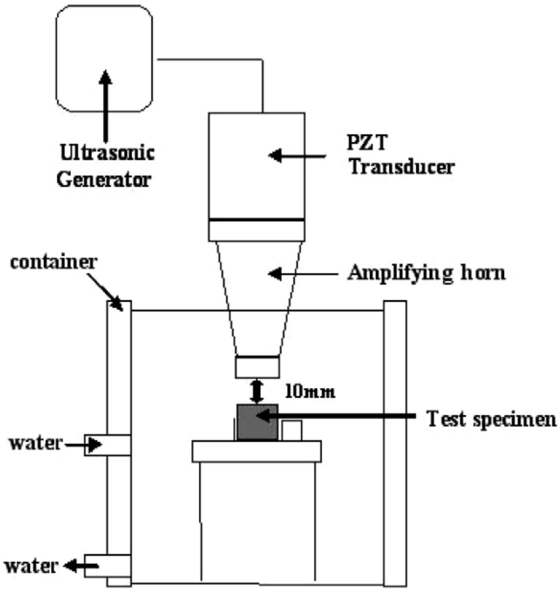

Fig. 1. Schematic representation for vibratory cavitation erosion test equipment.

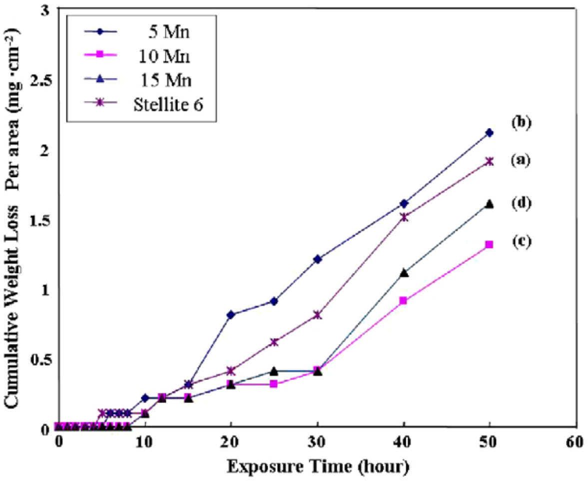

Fig. 2. Compare the cumulative weight loss of Stellite 6 and Fe–Cr–C–Si–$x$Mn ($x = 5$, 10 and 15 wt%) alloys as a function of exposed time: (a) Stellite 6, (b) 5 wt% Mn, (c) 10 wt% Mn and (d) 15 wt% Mn.

Table 1
Nominal elemental composition of the hardfacing alloys (wt%)

| Element | Co | Fe | Ni | Cr | Mn | Si | W | Mo | C |
|---|---|---|---|---|---|---|---|---|---|
| Stellite 6 | 60 | 2.09 | 2.21 | 29 | 0.61 | 0.81 | 4.68 | 0.59 | 1.25 |
|  | – | 70 | – | 20 | 5 | 1.0 | – | – | 1.7 |
| Mn added Fe base | – | 65 | – | 20 | 10 | 1.0 | – | – | 1.7 |
|  | – | 60 | – | 20 | 15 | 1.0 | – | – | 1.7 |

To the best of our knowledge, we have not found any quantitative and theoretical results concerning the stacking fault energy of the Mn added Fe-based alloy as a function of the Mn content. However, it is generally described that the increasing Mn content in the Fe-based alloy tends to lower the stacking fault energy, preventing recombination of partial dislocations necessary for cross slip and thus planner slip is the predominant mode of deformation. This results in reduced dislocation interactions at grain and twin boundaries that are the major barrier to dislocation movement reduction of ductility that are associated with an increase of resistance to erosion.

The respective cumulative weight losses of 5, 10 and 15 wt% Mn added alloys and Stellite 6 were roughly 2.1, 1.3, 1.6 and 1.9 mg mm$^{-2}$ after exposure of 50 h. Hence, additions of Mn exceeding 10 wt% alloys showed improved cavitation erosion characteristics compared with that of Stellite 6.

The surface morphology of all the tested alloys were observed using an optical microscope before and after the exposure to cavitation for 5, 10 and 20 h and is shown in Fig. 3. In the case of 10 and 15 wt% Mn added alloys, the crack was initiated in the carbide with increasing exposure time although the matrix region adjacent to the carbide was hardly damaged. The specimen after the 5 h cavitation erosion test showed minor cracks at the interfaces between matrix and carbide. During the incubation time, no noticeable damage was observed by cavitation erosion. On the contrary, the 5 wt% Mn added alloy exhibited a large material loss and showed that cracks propagated relatively easily through the matrix region.

In the Fe-based alloys with the austenitic structure, the cavitation erosion resistance was considered to be dependent on the stacking fault energy, the twinning, and the phase transformation [6]. It is also well known that for austenitic Fe-based alloys with very low stacking fault energies, martensite can be formed by strain-induced martensitic transformation during plastic deformation: the fcc → hcp strain-induced martensitic transformation in Stellite alloys, and both $\gamma \rightarrow \alpha'$ and $\gamma \rightarrow \varepsilon$ strain induced martensitic transformations in austenitic Fe base alloys [7].

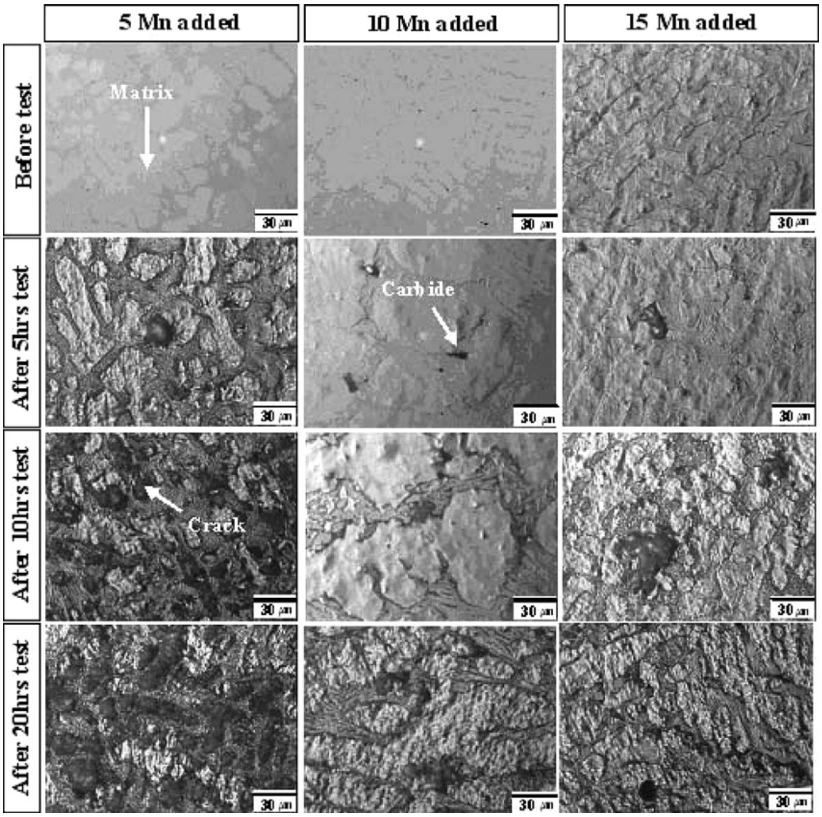

Fig. 3. Optical micrographs of cavitation erosion surfaces of Fe–Cr–C–Si–$x$Mn ($x = 5$, 10 and 15 wt%) alloys.

X-ray diffraction patterns of the tested samples before and after the exposure to cavitation are shown in Fig. 4. In the case of the 5 wt% Mn alloy, the $\gamma \rightarrow \alpha'$ strain-induced martensitic transformation was dominant at the low manganese content, however the addition of manganese above 10 wt% seemed to promote the formation of strain-induced $\varepsilon$ martensite. The strain-induced $\alpha'$ martensite is formed from shear band intersections, such as stacking faults, twins, and $\varepsilon$ martensite platelets [8].

Schumann and Doherty [9] established that a high-Mn alloy can be defined as an alloy containing more than 10 wt% Mn that formed strain induced $\varepsilon$ martensite during cavitation erosion. The strain-induced $\varepsilon$ martensite is formed by a simple mechanism, the passage of partial dislocations. This means that $\gamma \rightarrow \varepsilon$ strain-induced martensite can be relatively easily generated because of its simpler formation mechanism compared to the $\gamma \rightarrow \alpha'$ strain-induced martensite during the cavitation erosion test. Therefore, it was conjectured that the $\gamma \rightarrow \varepsilon$ strain-induced martensitic transformation would lead to an increased martensite fraction and be more beneficial than the $\gamma \rightarrow \alpha'$ strain-induced martensitic transformation owing to the blocking of dislocation motion and subsequent increase in hardness of the matrix by work hardening.

As shown in the XRD analysis results and material loss by cavitation erosion, although both 10 and 15 wt% Mn specimens incurred the strain-induced $\varepsilon$ martensite phase transformation; the cavitation erosion behavior of 15 wt% Mn specimens is worse than that of 10 wt% Mn specimens. Fig. 5 shows the microstructure of the 10 and 15 wt% Mn added Fe-based alloys exposed to cavitation. The carbide volume fraction of 10 and 15 wt% alloys was approximately 28.7% and 37.5%, i.e., the carbide volume for 10 wt% Mn was less than that for 15 wt% Mn.

According to Sapate [10] the erosion rate increases with increasing volume fraction of carbides. Because the matrix hardened by strain-induced phase transformation effectively repressed the crack propagation, the cavitation erosion around the carbide area mainly dictates the wear behavior. Therefore, the enhanced cavitation

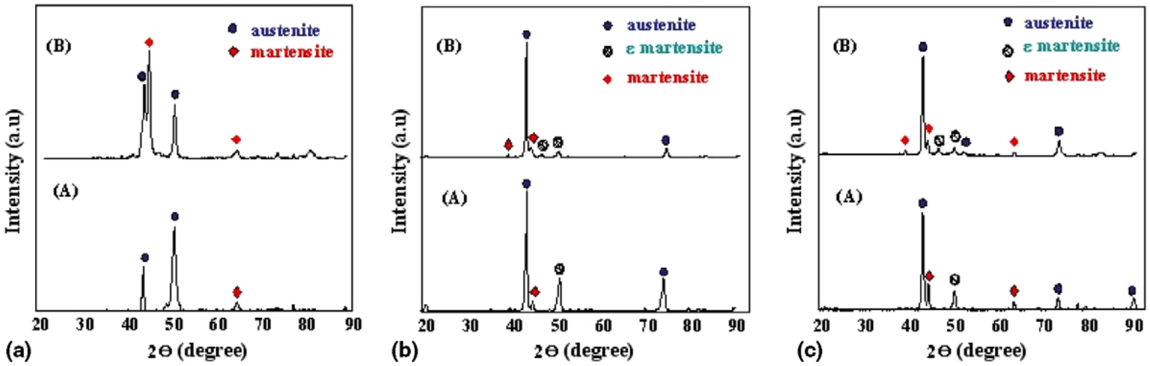

Fig. 4. X-ray diffraction patterns of (a) 5 wt% Mn, (b) 10 wt% Mn, (c) 15 wt% Mn: (A) before and (B) after the exposure to cavitation.

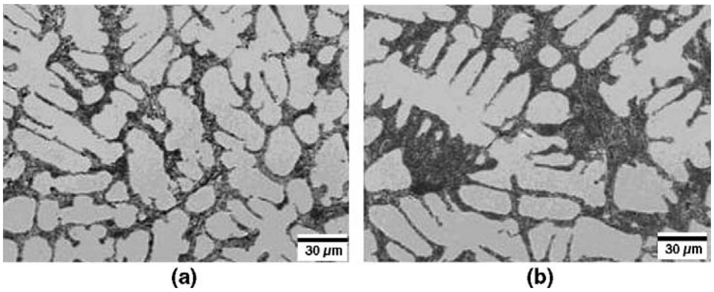

Fig. 5. SEM micrographs of cavitation erosion surfaces: the carbide volumes of (a) 10 wt% Mn and (b) 15 wt% Mn.

erosion resistance of the 10 wt% Mn alloy over the 15 wt% Mn alloy could be related to the reduction in the carbide volume fraction.

## 4. Conclusions

1. The enhanced cavitation erosion resistance of the Mn added Fe-based alloys, superior to the traditionally used Stellite 6, was attributed to the hardened matrix that could suppress the propagation of cracks initiated at carbide-matrix interfaces and the reduction of the carbide volume fraction.
2. Additions of manganese exceeding 10 wt% improved the cavitation erosion resistance of the Fe-based alloy. The improvement is likely due to the development of the $\gamma \rightarrow \varepsilon$ strain induced martensitic transformation.
3. The $\gamma \rightarrow \varepsilon$ strain induced martensitic transformation is considered to be more beneficial to the cavitation erosion resistance of Fe-based alloys than the $\gamma \rightarrow \alpha'$ strain-induced martensitic transformation due to the high work-hardening rate.
4. Erosion resistance of the 15 wt% Mn added Fe-based alloy was worse compared with the 10 wt% Mn added alloy. The erosion rate increased due to the larger carbide volume in the 15 wt% Mn alloy. Hence, the critical Mn content for optimal erosion resistance lies in the 10–15 wt% Mn range.

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