Yttrium molybdates coating deposition of oxide-fibre/molybdenum-matrix composites

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Abstract. Shown a possibility to do a coating process on void-free surfaces which based on Yttrium molybdate on composite including molybdenum matrix by using ion-plasma deposition. Reported results of X-ray phase analysis of coating before and after annealing and also results of a microstructure analysis.

1. Introduction

The development of high temperature materials beyond both nickel superalloys and modern niobium alloys described in a series of the publications aims at molybdenum alloys in the Mo-Si-B systems [1, 2] and molybdenum-matrix fibrous composites [3, 4]. The behavior of fibrous metal matrix composites differs from that of metal alloys: fracture toughness and strength of the composites can go up simultaneously by increasing the volume fraction of strong brittle fibres [5, 6]. The alloys are characterized by a conflict between strength and fracture toughness. Molybdenum alloys in the Mo-Si-B system developed have high strength and creep rupture properties up to 1300 °C, sufficiently good oxidation resistance up to 1200 °C [5]. Coatings on the surface of specimens of such alloys to enhance the oxidation resistance at temperatures up to 1300 °C are also known [6]. However, fracture toughness of these alloys is too low to use them in heavily loaded structural elements [5].

Hence, molybdenum matrix fibrous composites should also be considered as a possible family of heat resistance materials. An interest of the present authors for oxide fibre/molybdenum-matrix composites was stimulated by (i) an effective way to produce such composites called the internal crystallization method (ICM) and (ii) an observation of a reduced oxidation rate of the molybdenum matrix provided it is reinforced with a fibre of a special chemical composition [5, 6]. Such composites are characterised by high strength and high creep resistance at temperatures up to about 1300 °C [5, 6]. In particular, if the reinforcing fibre contains Me (Me = yttrium or lanthanide) then molybdates of Me occur on the surface of a composite specimen that prevents rapid oxidation of molybdenum. The molybdates can be healing agents for defects in a coating that can arise in the service of the composite.

Therefore, the technology of coating the composites by molybdates is to be developed. In the present paper, yttrium molybdates coatings on molybdenum-matrix composites reinforced with the yttrium-aluminium perovskite (YAP) were deposited by ion-plasma method described in [3]. It is important to stress out that the information on yttrium molybdates is very scarce. There are a number
of the compounds in the Y$_2$O$_3$ – MoO$_3$ phase diagram including Y$_2$O$_3$·3MoO$_3$ (Y$_2$Mo$_3$O$_{12}$) with melting point 1310 °C, Y$_2$O$_3$·MoO$_3$ (Y$_2$MoO$_6$) and 3Y$_2$O$_3$·MoO$_3$ (Y$_6$MoO$_{12}$) [6]. Note that the melting points of the last two compounds are not determined but they took to be much higher than 1310 °C.

2. Experimental methods

Preliminary experiments to determine coating parameters and regimes were conducted with a 18-10 stainless steel substrate. Then composite specimens with molybdenum matrix and fibres based on YAlO$_3$ (YAP) were coated. The YAP-based-fibre/Mo-matrix composites were chosen as they are characterised by sufficiently high strength at temperatures up to 1400 °C and good fracture toughness properties. Coating was performed by using the ion-plasma technique, the corresponding equipment is shown schematically in figure 1. The apparatus allows coatings with either pure metals or compounds like nitrides, carbides, oxides of various metals.

Figure 1. Schematics of the coating equipment.

The deposition of yttrium molybdates was carried out by using molybdenum and yttrium cathodes. To obtain yttrium molybdates of various stoichiometric compositions (Y$_2$Mo$_3$O$_{12}$, Y$_2$MoO$_6$ and Y$_6$MoO$_{12}$) three deposition regimes were developed. To provide an adhesion of the coating to molybdenum matrix the process started with depositing thin molybdenum sub-layer, which was done in argon gas atmosphere for 5 minutes. Then oxygen lets to the chamber and according regime switched on for 60 min to deposit one of the molybdates mentioned.

The phase analysis of the coatings was performed by X-ray diffractometer Rigaku Ultima equipped with the Cu-Kα radiation source; the range of angles 10–100°. The wavelength = 1.540562 Å, the survey step was 0.02°. Analysis of the X-ray spectra was carried out by using software Match! Crystal Impact.

As mentioned above, the first experiments to find appropriate deposition regimes were conducted by using a steel substrate. The X-ray phase analysis of coated steel samples after deposition (figure 3) reveal an amorphous structure of the coated layer. Hence, the specimens were annealed at a temperature of 950 °C for 1 hour in air atmosphere to crystallise the coating. The X-ray spectra (figure 3) show that crystallisation has been really occurred. The Y$_2$MoO$_6$ compound predominated in the coating obtained according to deposition regime #1, and the Y$_2$Mo$_3$O$_{12}$ molybdate exists in the coating obtained according to regime #3.

For the metallographic examination of the coatings on composite specimens, there were prepared oblique cross-sections with the 6° angle between the cut plane and the longitudinal direction of a specimen. The morphology of the coatings was observed by scanning electron microscope JEOL JSM-
6390 operated in the secondary electron mode. The microscope was equipped with INCA Energy that allowed analyzing the distribution of chemical elements across the coating thickness.

3. Results and discussion
Investigation of the structure showed that the coatings obtained can be characterized as continuous, without cracks and stratifications. The microstructure of the coated samples for all modes has a similar structure. An electronic image of the micro-texture of the coating obtained by mode № 1 is shown in figure 2(a). Points "Spectrum 1-4" indicate the areas of local energy-dispersive analysis: Spectrum 1 – oxide fiber, Spectrum 2 – molybdenum matrix, Spectrum 3 – undercoat coating, Spectrum 4 – coating. Similar studies were carried out for other regimes. Table 1 shows the results of an energy-dispersive analysis of the corresponding spectra for three samples.

![Figure 2](image)

**Figure 2.** The SEM micrograph of the cross-section of a composite specimen with a coating obtained by regime #1.

**Table 1.** Chemical compositions of the composites and coatings obtained of EDS chemical micro analysis (at %).

| Mode №1  | O  | Al  | Y   | Mo  |
|----------|----|-----|-----|-----|
| Spectrum 1 | 48.34 | 22.86 | 28.80 |
| Spectrum 2 | 100.00 |       |       |
| Spectrum 3 | 47.70 | 41.81 | 10.49 |
| Spectrum 4 | 54.61 | 33.45 | 11.94 |

| Mode №2  | O  | Al  | Y   | Mo  |
|----------|----|-----|-----|-----|
| Spectrum 1 | 53.29 | 20.89 | 25.82 |
| Spectrum 2 | 100.00 |       |       |
| Spectrum 3 | 47.86 | 41.03 | 11.11 |
| Spectrum 4 | 50.71 | 41.70 | 7.59  |

| Mode №3  | O  | Al  | Y   | Mo  |
|----------|----|-----|-----|-----|
| Spectrum 1 | 53.41 | 20.84 | 25.75 |
| Spectrum 2 | 100.00 |       |       |
| Spectrum 3 | 47.93 | 14.74 | 37.33 |
| Spectrum 4 | 66.18 | 6.85  | 26.98 |
The composition of yttrium molybdates $Y_2MoO_6$, $Y_2MoO_6$ and $Y_2MoO_6$ is analyzed by the ratio of yttrium and molybdenum (the method does not allow determining the oxygen content with sufficient accuracy) (table 1, Spectrum 4 for all modes). The results of the analysis with indication of deviations from stoichiometric compositions are given in table 2.

**Table 2.** Correlation of coating compositions with stoichiometric compositions of yttrium molybdates.

| № Mode | Yttrium molybdates | Deviation, at. % |
|--------|--------------------|------------------|
| 1      | $Y_2MoO_6$         | 9.5              |
| 2      | $Y_2MoO_12$        | 3.9              |
| 3      | $Y_2MoO_12$        | 11.2             |

The distribution of the elements along the line for mode № 1 is shown in figure 3. Comparison of electronic images and diagrams of distribution of the elements demonstrates the presence of a diffusion layer between the matrix material and the sublayer and the coating and the sublayer. So, for example, to cover the diffusion layer obtained by the mode №1 (figure 3(a), (b)), it is located between the 90 and 120 μm marks along the abscissa axis of the element distribution diagram; the sublayer is between 120 and 180 μm, followed by the main coating.

X-ray phase analysis of coated steel samples prior to annealing showed that the coating has an amorphous structure – only the substrate peaks (08H18N10 steel) and amorphous halos belonging to the coating material are present on the diffractograms (figure 3(a), (b)).

![Figure 3](image)

**Figure 3.** Diffractograms of coated steel samples before and after annealing obtained by mode: (a) – № 1; (b) – № 2.

To stabilize the structure of the coating, the samples were heated at 950 °C for 1 hour in an air atmosphere. The diffractograms of the coated steel samples after annealing are shown in figure 3.

Annealing for 1 hour resulted in the crystallization of yttrium molybdates in the coating, as evidenced by the presence of corresponding peaks. The $Y_2MoO_6$ compound predominates in the coating obtained according to the mode № 1, and $Y_2MoO_15$ according to the mode № 3. Peaks belonging to iron, chromium and nickel oxides in the first and second coatings were not detected. In the coating obtained by the mode № 2 there are peaks of iron oxide, which indicates the oxidation of the substrate, and therefore a shorter-term practical application of the coating obtained under this mode. The possibility of using coatings obtained by the modes № 1 and № 3 requires additional studies.

The X-ray phase analysis showed that when coatings are formed from two one-component cathodes made of Mo and Y in an oxygen atmosphere at a temperature of the processed sample not exceeding 500 °C, chemical compounds of yttrium molybdates of different phase composition are
synthesized on the surface. Thus, there has been developed a fundamentally new method for forming coatings based on yttrium molybdates.

**4. Conclusion**
1. Based on the results of the research, it has been shown it is possible to apply continuous coatings on the basis of molybdates of yttrium by ion-plasma spraying on a composite with a molybdenum matrix. The thickness of the coatings obtained is about 35 μm.
2. There is developed a method for forming coatings based on yttrium molybdates from a vacuum-arc discharge plasma of the required stoichiometric composition.
3. Immediately after application, the coating material has an amorphous structure that acquires a crystalline structure after annealing at a temperature.
4. Based on the data of X-ray phase analysis, it can be concluded that the most prospected, from the point of view of practical application, are the coating obtained according to the modes № 1, № 2.

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