EFFECTS OF COPPER AND SULFUR ON REFRACTORY-METAL SILICIDING
AND THE PROPERTIES OF DIFFUSION COATINGS

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Studies have been made on the effects of copper and sulfur on the structure formation, phase formation, and growth of silicide coatings on refractory metals.

Diffusion siliciding of metals and alloys differs from other such treatment methods in involving a simple technology and extensive applications. On the other hand, the method has a substantial disadvantage in being very lengthy. Additives are used to intensify the process, which contain about 80% of added component and up to 10% of fluoride activator [1-4]. However, this leads to a considerable increase in the cost of the process and the production of fluoride effluents.

A promising means of reducing the siliciding cost for refractory metals is to use a powdered additive having a low silicon content, which provides for forming a high-quality coating on the metal, but one of small thickness [5]. One can increase the activity of the treatment medium by adding components that not only act as activators but also enhance the physicochemical properties of the protective layer [6-8]. The one-component additives that can be used with the powder mixture include particularly copper and sulfur. These elements form readily fusible eutectics during the silicon treatment, which participates in producing the silicide layers [9]. It is therefore important to establish the effects of copper and sulfur on the structure formation and phase formation as well as on the growth of the silicide coatings and the properties of them.

Tests have been done on refractory metals (niobium, tantalum, molybdenum, and tungsten) treated with silicon at 950-1100°C in mixtures containing 40% silicon, 1% sodium fluoride, and from 1 to 10% copper powder, balance aluminum oxide, which have shown that niobium and tantalum form two-layer coatings. Microprobe analysis shows that the outer layer of the coating is the refractory-metal disilicide MeSi₂, while the inner one is the lower silicide Me₅Si₃. There are also changes in the coating structure. The outer layer of a silicide coating on niobium or tantalum is composed mainly of small acicular crystals, whose sizes increase with the copper content in the powder mixture. The microhardness of the MeSi₂ silicide phases is 20-30% lower than that of silicide layers formed without the participation of copper [10].

Molybdenum and tungsten differ from niobium and tantalum in producing single-phase coatings: refractory-metal disilicide. The structure consists of small acicular crystals, and only at the outer boundary of the silicide phase is there a thin zone of randomly oriented crystals whose thickness increases with temperature and time. For example, after 12 h at 1100°C, the zone of disoriented crystals occupies over 2/3 of the thickness of the coating, and at the centers there are large crystals of the disilicide. At the inner boundary of the coating (MeSi₂-Me), there is a zone of columnar crystals oriented into the metal, whose thickness increases with time. The microhardnesses of the silicide layers on molybdenum and tungsten are 40-50% lower than those of disilicide phases formed in mixtures not containing copper [10]. As the copper content in the siliciding mixture increases, there is a substantial increase in the growth rate of the coating on the refractory metal (Fig. 1). However, as the coating thickness increases, the following effect occurs: there is an increase in the number and width of the radial cracks together with a tendency to detachment from the metal substrate. Also, the thickness of the Me₅Si₃ phase increases on niobium and tantalum. To produce a high-quality silicide coating on a refractory metal, it is best to use a mixture in which there is not more than 10% copper.

We examined the effects of temperature on refractory-metal siliciding for a mixture containing 5% copper. The process was an accelerating one in the temperature range 950-1100°C. The thickness of the coating layer increased by a

*Here and subsequently, mass proportions of components.

Fig. 1. Effects of copper content in mixture on the thickness of the silicide coatings on refractory metals: $T = 1050^\circ C$, $\tau = 6$ h; 1) tungsten; 2) molybdenum; 3) niobium; 4) tantalum.

Fig. 2. Photomicrographs of silicon coatings on molybdenum, $T = 1100^\circ C$, $\tau = 6$ h (200 x 200 $\mu$m) $\times$ 2000: a) absorbed-electron pattern; b, c, and d) in x rays of silicon, molybdenum, and copper.