JOURNAL OF MATERIALS SCIENCE 11 (1976) 246–250

Aligned Co-Co_2 Si eutectics

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The addition of W, Ta, or Al to Co-rich Co–Si alloys suppresses the formation of Co_3Si and produces stable eutectics between the Co_2Si and the Co-rich solid-solution phase. The Co–Si–W and Co–Si–Ta alloys solidified as three-phase eutectics. The Co–Si–Al alloy solidified as a two-phase eutectic, but a third phase precipitated on cooling. Interesting morphological changes were produced by epitaxial precipitation of Co_2Si from solid solution during cooling.

1. Introduction
Directional cooling of Co–25 at.% Si can produce solidification of single-phase Co_3Si and subsequent eutectoid decomposition of this phase into an aligned lamellar composite of Co_2Si and Co(Si) solid solution [1–3]. This aligned eutectoid has been found to have promising tensile properties at elevated temperatures [3].

In some cases, it was found that nucleation of Co_3Si did not immediately occur, allowing Co_2Si and Co(Si) to solidify together as a metastable lamellar eutectic [3–5]. This eutectic consisted of the same phases as the eutectoid, but had a much larger lamellar spacing because phase separation occurred by liquid-state rather than solid-state diffusion.

In an attempt to improve the mechanical properties of Co–Co_2Si aligned eutectoid, the effects of various alloying elements on microstructure and properties have been studied. With alloying elements similar to Co in atomic number and radius (Cr, Mn, Fe, Ni, and Cu), eutectoid microstructures were maintained, although alignment and mechanical properties deteriorated [6]. We report here the effects of adding alloying elements very different from Co in atomic number and radius, i.e., W, Ta, and Al.

2. Experimental
The initial compositions studied were 25 at.% Si, 70 at.% Co, and 5 at.% M, where M was either W, Ta, or Al. Samples about 0.42 cm diameter and about 10 cm long were directionally solidified and transformed at 0.64 cm hr^{-1} down a temperature gradient of about 300° C cm^{-1}.

Longitudinal and transverse sections were studied by light metallography. The etchant used was either 10 parts HNO_3, 10 parts HF, and 30 parts glycerine or 10 parts HNO_3, 20 parts HCl, and 30 parts glycerine. Average compositions at various positions along the sample were measured by chemical analysis, and local compositions of various phases were determined by electron microprobe analysis.

3. Results
3.1. Co–Si–W
The initial portions of the ingot containing 5 at.% W had a complex microstructure containing dendritic phases. However, after several cm of growth, an aligned lamellar structure was formed (Fig. 1). The lamellar spacing was greater than 10 μm, indicating this to be a eutectic, rather than a eutectoid, microstructure [3].

Chemical analysis at various positions along the ingot indicated compositional changes produced by directional solidification, and the final portion to freeze was found to have an approximate composition of 24 at.% Si, 74 at.% Co, and 2 at.% W. An alloy of this composition was subsequently cast and directionally solidified under the same conditions of temperature gradient and growth rate. The entire length of the sample consisted of dendrite-free aligned structure similar to Fig. 1. It was concluded that this composition was at or near a eutectic composition.

The unusual serrated form of the lamellae (Fig. 1b) was found, from study at higher magnification,

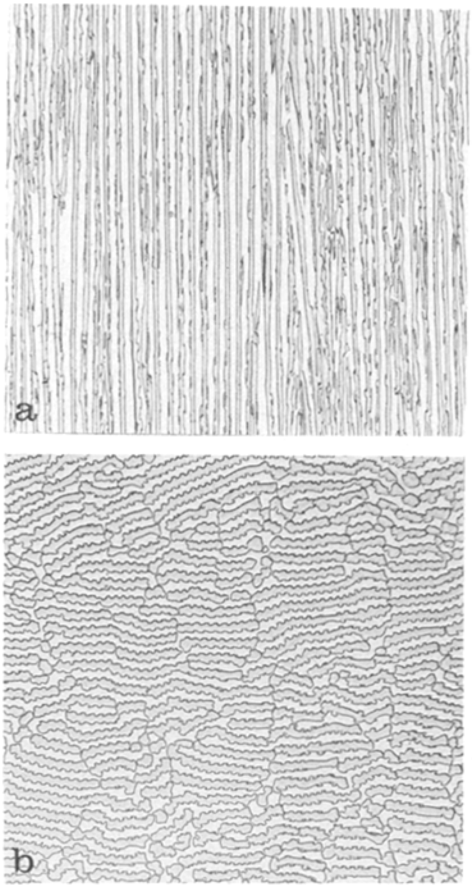

Figure 1 Structure of directionally-solidified Co–Si–W alloy. (a) Longitudinal section, growth direction vertical, × 150. (b) Transverse section × 375.

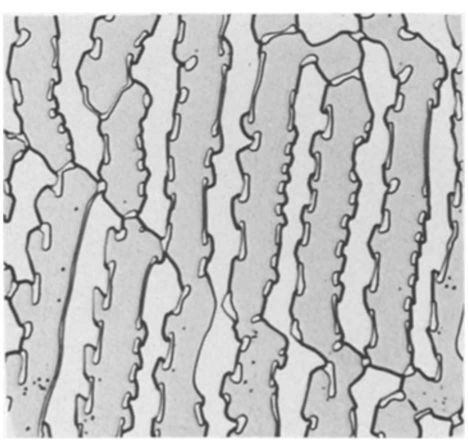

Figure 2 Higher magnification of transverse section of Co–Si–W alloy. Grey lamellae are Co_2Si, white lamellae are Co-rich solid solution, and third phase is Co_3W_2Si, × 1250.

to be related to the presence of a third phase (Fig. 2). Microprobe analysis showed that the grey lamellae were Co_2Si containing only 0.6 at.% W, and the white lamellae were Co containing 15 at.

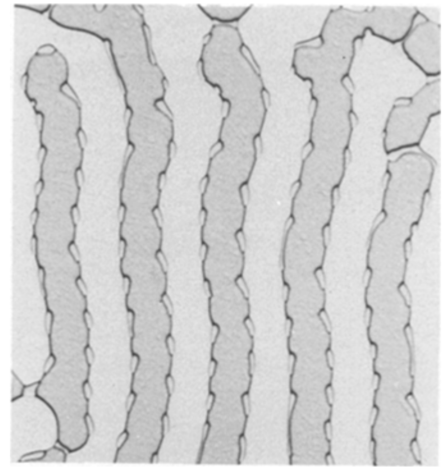

Figure 3 Transverse section of Co–Si–W alloy after quenching from 1100° C. Comparison with Fig. 2 indicates that serrated Co–Co_2Si interface resulted from growth of Co_2Si phase during cooling, × 1250.

% Si and 1.7 at.% W. The third and minor phase had an approximate composition of 54 at.% Co, 27 at.% W, and 19 at.% Si, and probably corresponds to the λ_1 phase found by Russian investigators and designated as Co_3W_2Si [7].

The irregular shape of the Co–Co_2Si interface does not appear to be an equilibrium form. A sample heated to 1100° C for 2 h and quenched into water showed a much less serrated phase boundary (Fig. 3). It was concluded that the as-solidified microstructure was similar to that of Fig. 3, but that a decreasing solubility of Si in Co with decreasing temperature led to a growth of the Co_2Si phase by epitaxial precipitation during cooling. The growing Co_2Si phase bowed between, and in some cases partly enveloped, the λ_1 particles along its initial boundary, producing the striking serrated forms of Figs. 1 and 2.

3.2. Co–Si–Ta

The initial portions of the ingot containing 5 at.% Ta had a dendritic structure, but after several cm of growth a non-dendritic, complex three-phase structure was formed (Fig. 4). Again the interphase spacings were characteristic of a eutectic, rather than a eutectoid, structure.

Chemical analysis indicated segregation produced by freezing, and the final portion to freeze had an average composition of approximately 22.3 at.% Si, 74 at.% Co, and 3.7 at.% Ta. An alloy of this composition was cast and directionally solidified and transformed under the same conditions. The entire length of the sample con-

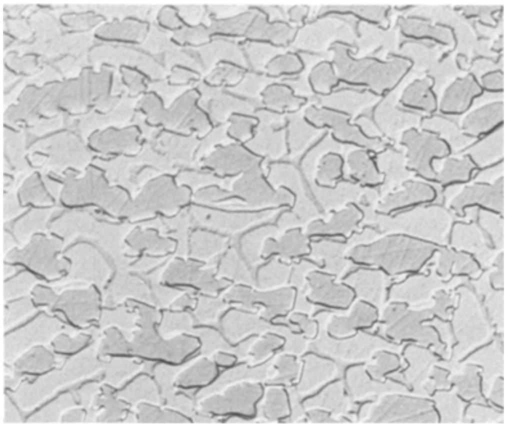

Figure 4 Transverse section of directionally-solidified Co–Si–Ta alloy. Irregular grey rods are Co_2Si, light matrix is Co-rich solid solution, ribbon-like phase is $Co_{16}Si_7Ta_6$, × 750.

sisted of dendrite-free aligned structure similar to Fig. 4. It was concluded that this composition is at or near a eutectic composition.

Microprobe analysis of the separate phases indicated that the irregular grey rods were Co_2Si, and the light matrix Co with 12 at. % Si, neither phase containing detectable Ta. All the Ta appeared to be in the third, ribbon-like phase in the matrix which ran between neighbouring Co_2Si rods. The approximate composition of this phase was 58 at. % Co, 26 at. % Si, and 16 at. % Ta. Considering the inaccuracy of analysis with such thin phases, we identify this phase with the ternary compound $Co_{16}Si_7Ta_6$ or G-phase reported by Spiegel *et al* [8].

A sample heated for 2 h at 1100° C and water-quenched showed the same phases in roughly the same configuration, but the cross-sections of the Co_2Si rods were much less irregular. It was concluded that here, as in the Co–Si–W alloy, the Co_2Si phase grows during cooling, producing some of the complexity of shape seen in Fig. 4.

3.3. Co–Si–Al

The entire length of the ingot containing 5 at. % Al contained dendrite-free eutectic-like structure, partly lamellar and partly rod. A transverse section of the rod structure is shown in Fig. 5. As with the Co–Si–W and Co–Si–Ta, the structure contained a third phase.

Microprobe analysis showed that the grey rod phase was Co_2Si containing only 1.5 at. % Al. The matrix and third phase together had an average composition of 73 at. % Co, 15 at. % Si, and 12 at.

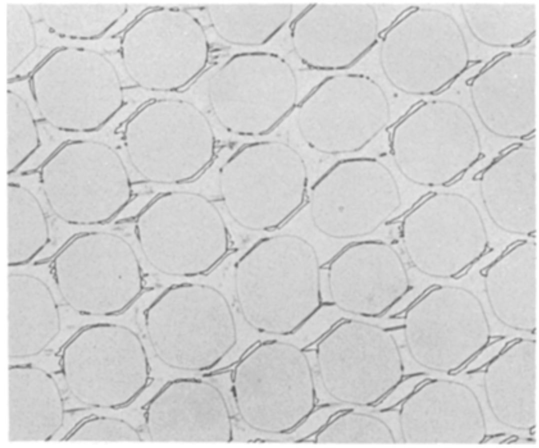

Figure 5 Transverse section of directionally-solidified Co–Si–Al alloy. Grey rods are Co_2Si, light matrix is Co-rich solid solution, and third phase is believed to be CoAl, × 940.

% Al. Because of the fine dimensions of the third phase, an accurate composition could not be determined. However, it had a higher Al content than the matrix, and it is believed to be CoAl, probably containing some Si.

The large volume fraction of Co_2Si rods suggests that there has been considerable growth of the Co_2Si phase on cooling, since rod microstructures are expected to solidify only for volume fractions less than about 30%. As in the Co–Si–W and Co–Si–Ta alloys, this growth presumably occurred by epitaxial precipitation from solid solution. Accepting this, the location of the third phase on the circumference of the Co_2Si rods indicates that

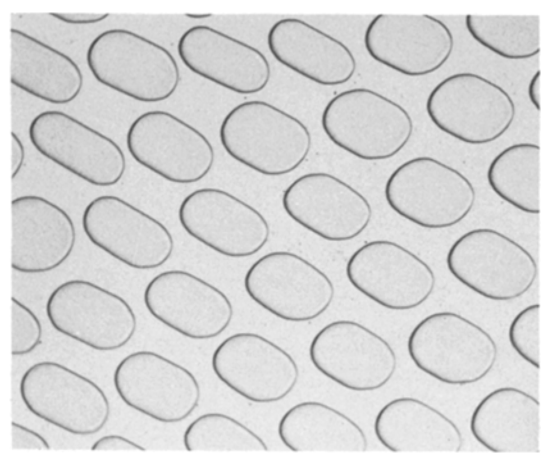

Figure 6 Transverse section of Co–Si–Al alloy quenched from 1100° C. Comparison with Fig. 5 indicates that Co_2Si phase grew during cooling, and that the third phase was not present after solidification, but precipitated from solid solution during cooling, × 940.

this phase was not present on solidification, but precipitated from the matrix *after* most of the Co_2Si had precipitated, i.e. at a lower temperature.

This conclusion was tested by heating a sample for 2 h at 1100° C and quenching in water. The resulting structure (Fig. 6) shows a smaller volume fraction of Co_2Si and an absence of the third phase. This structure is presumably more nearly representative of the as-solidified structure, and proves that the third phase formed by solid-state precipitation rather than solidification.

4. Discussion

According to the phase diagram of van den Boomgaard and Carpay [1], the phase Co_3Si is stable only from its melting point of 1210° C to its eutectoid decomposition temperature of 1170° C, below which it decomposes into Co_2Si and Co(Si) solid solution. As a result of this marginal stability of Co_3Si, under some experimental conditions it is possible to avoid its formation and produce Co_2Si and Co(Si) directly from the melt as a metastable eutectic [3–5]. However, it is difficult to produce samples of substantial size consisting only of this metastable eutectic, since it becomes unstable once the stable phase Co_3Si is formed.

The present results indicate that some alloying elements, specifically W, Ta, and Al, can suppress the formation of the Co_3Si phase and thereby produce stable eutectics between the Co_2Si and Co(Si) phases. These alloying elements apparently raise the free energy of the Co_3Si phase relative to these two other phases, and thereby eliminate the narrow temperature range of stability of Co_3Si. As a result, eutectic rather than eutectoid structures are produced. Although the larger interphase spacings of eutectics lead to lower strengths in the Co–Si binary alloys [3], this effect can be compensated for by the strengthening produced by alloying elements [6]. Further study of Co–Co_2Si eutectics as the basis of high-temperature structural alloys may therefore be worthwhile.

All three alloying elements studied produced three-phase microstructures. It was shown by quenching from 1100° C that in the Co–Si–Al alloy the third phase formed not by solidification, but by precipitation from solid solution during cooling. In the Co–Si–W and Co–Si–Ta alloys, on the other hand, all three phases apparently formed directly from the melt as true ternary eutectics.

Also of interest were the morphological changes produced by epitaxial precipitation of Co_2Si from the Co-rich solid solution during cooling. This precipitation led to a large volume fraction of rods in the Co–Si–Al alloy (Fig. 5), and to irregular rod shapes in the Co–Si–Ta alloy (Fig. 4). The effects in the Co–Si–W alloy were particularly interesting because of the presence of third-phase rods along the initial interface between the Co_2Si and solid-solution phases (Fig. 3). These rods pinned the interface, and the growth of the Co_2Si during cooling therefore required a bowing of the interface (Fig. 2) and produced a striking serrated microstructure (Fig. 1)

Finally, it should be noted that the third phase occurred preferentially at the interface between the Co_2Si and the solid solution in the Co–Si–W and Co–Si–Al alloys, but mostly within the solid-solution matrix in the Co–Si–Ta alloy. This difference presumably resulted from a difference in the relative energies of the various interphase interfaces.

5. Summary

The addition of W, Ta, or Al to Co-rich Co–Si alloys suppressed the formation of Co_3Si and produced stable eutectics between the Co_2Si and Co-rich solid-solution phases. Directional solidification produced aligned structures. In the Co–Si–W and Co–Si–Ta alloys, true three-phase ternary eutectics were formed. The Co–Si–Al alloy solidified as a two-phase eutectic, but a third phase precipitated from solid solution during cooling. Interesting morphological changes were also produced by epitaxial precipitation of Co_2Si during cooling.

Acknowledgements

Alloys were directionally solidified by Craig Palmer. Metallography was done by Barbara Beach, and microprobe analysis by Mal McConnell and Fred Bacon. This work was supported in part by the Naval Air Development Center.

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Received 9 July and accepted 29 July 1975.