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Effects of alloy additions on the microstructures and tensile properties of cast Co–Cr–Mo alloy used for surgical implants

L. Z. ZHUANG, E. W. LANGER
Department of Metallurgy, Technical University of Denmark, DK-2800 Lyngby, Denmark

The composition of the Co–Cr–Mo alloy has been modified by additions of nickel and some trace elements aluminium, titanium and boron. In this paper, the first part of the present study, the effects of alloy additions on the microstructures and tensile properties of the as-cast Co–Cr–Mo alloy are discussed. The effects of alloy additions on the fatigue behaviour of the alloy will be discussed in the second part of the present study. It is found that alloy additions do not seem to result in changes in the nature of the casting structure. A directional, coarse dendritic cast structure is produced in the modified alloys as in the base alloy. However, the alloy additions affect the carbide precipitations and the formation of some fine details of the microstructure such as dislocations, stacking faults and twins produced during the solidification. A considerable improvement in the transient mechanical properties, especially in the tensile ductility, is achieved by modifying the base alloy with alloy additions.

1. Introduction

Cast Co–Cr–Mo alloy has been used for many years as a surgical implant material because it offers a suitable combination of corrosion resistance and mechanical strength. Even today it remains popular and it is estimated that more than half of the currently used total hip replacement appliances are cast in Co–Cr–Mo alloy. At present, however, concern is being expressed as to the low ductility and fatigue strength of this alloy in the as-cast condition [1–7], which is felt to be responsible for the occasional failures of some implant devices [8–10].

Numerous approaches have been used to improve the mechanical properties, especially the fatigue properties, of the Co–Cr–Mo alloy [1, 11–27] and most of them have been shown to be satisfactory. The elimination of casting defects by thermo-mechanical treatment provides a means of improving the mechanical properties of the alloys. For instance, major improvements are obtained by hot isostatic pressing of cast alloys. This closes and seals the shrinkage cavities. Even greater improvements are obtained by mechanical working of ingots, which breaks down the as-cast structure and refines the grain size while also eliminating the shrinkage cavities. Also, recently it was shown that the corrosion fatigue resistance of the Co–Cr–Mo alloys may be substantially improved by powder metallurgy processing, using hot isostatic pressing to compact prealloyed powders. There are many other structural factors which also affect the mechanical behaviour of the Co–Cr–Mo implant alloys, including dispersed phases such as carbides, the density and distribution of dislocations, stacking faults and twins, as well as some phase transformations corresponding to the heat-treatment procedures. Therefore, various heat-treatment schemes also provide the microstructural changes responsible for the enhancement of the mechanical properties in the cast Co–Cr–Mo alloys. Furthermore, the effects of element additions on the microstructures and mechanical properties of the cast Co–Cr–Mo alloys and the mechanical property improvements resulting from some surface treatment processes, such as chemical or physical surface-coating techniques, have also been investigated.

In the present study, the composition of the Co–Cr–Mo alloy has been modified by additions of nickel and some trace elements such as aluminium, titanium and boron. In this paper, the first part of the present study, we draw the attention to the effects of alloy additions on the microstructures and tensile properties of the as-cast Co–Cr–Mo alloy. The effects of alloy additions on the fatigue behaviour of the alloy will be discussed in a following paper. Changes in the stacking fault energy (SFE) caused by nickel additions and the effects of SFE on the mechanical properties, especially on the fatigue properties, has been taken into consideration.

2. Materials and experimental procedure

Cast Co–Cr–Mo alloy, commercially known as Vitallium or H.S. 21 and its modified versions with alloy additions of nickel and some trace elements aluminium, titanium and boron were studied. The chemical compositions of the alloys are shown in Table I. Alloys were prepared by vacuum induction melting and cast in sand moulds with air cooling.

Individual castings were produced with the dimensions of 85 mm × 20 mm × 30 mm. All the specimens

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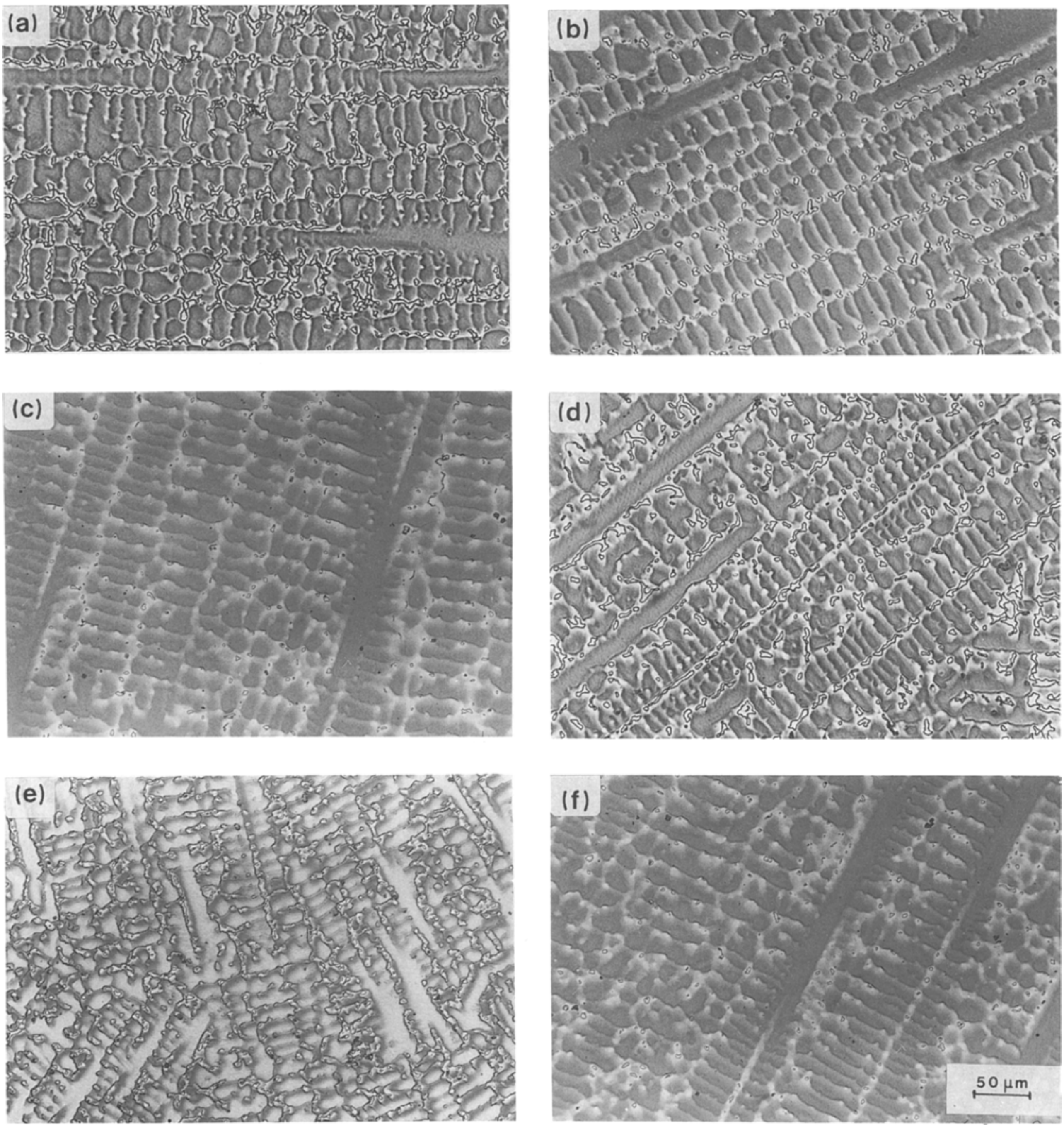

Figure 1 As-cast microstructures of the base alloy and the modified alloys showing a dendritic structure with interdendritic precipitation: (a) to (f) corresponding to alloys 1 to 6 with various compositions listed in Table I. Electrolytically etched with 60% HNO_3 + 40% H_2O.

were mechanically tested and structurally examined in the as-cast condition.

Metallographic specimens were prepared by mechanical polishing and electrolytic etching with etchant: 60% HNO_3 + 40% distilled water by volume, 10 to 25 sec at 5 V. Variations in chemical composition of the carbide precipitates caused by alloy additions were measured using EDS (energy dispersive spectroscopy) microanalysis in Philips SEM505 scanning electron microscope attached with EDAX equipment. Fresh fracture surfaces of tensile specimens were examined by scanning electron microscopy. Transmission electron microscopy was performed using disc-shaped specimens of 3 mm diameter. They were finally thinned by jet polishing in an electrolyte of 10% perchloric acid + 20% ethanol + 70% butanol by volume. Electrolyte temperature was maintained between -20 and $-30°$ C throughout thinning and at a potential of 30 V. The specimens were examined in Philips EM301 transmission electron microscope operating at 100 kV.

Microhardness measurements were made on polished surfaces using a load $p = 25$ gf. Tensile tests were performed at room temperature using an Instron testing machine (Model-1115) with a calibrated strain gauge extensometer. The strain rate in the elastic region during testing was $0.005\,\text{min}^{-1}$. Tensile specimens were cylindrical, machined to a dimension with a gauge length of 30 mm and a diameter of 6 mm from the original castings.

3. Results and discussion

Fig. 1 shows the microstructures of the as-cast alloys produced using sand moulds with air cooling and corresponding to the various compositions listed in Table I. It is seen that modifying the composition of the base alloy with additions of nickel and some trace elements such as aluminium, titanium and boron does not affect the nature of the casting structures in this alloy system. In all cases, a directional, coarse dendritic structure with interdendritic carbide precipitates is obtained in the modified alloys as in the base alloy. In addition, it is found that there is no obvious change in the grain size of the alloys resulting from the nickel additions into the base alloy. However, comparing the casting structures of the alloys with or without the additions of the minor trace elements aluminium, titanium and boron, it is indicated that a reduction in the grain size of about 5% to 10% is caused by the additions of these trace elements.

The addition of nickel to the base alloy affects the carbide precipitation behaviour significantly. It is observed that both the amount and the particle size, and therefore, the total amount of the carbide precipitates decrease strikingly with increasing nickel content in the alloys, as seen in Fig. 1. However, the additions of other minor trace elements, aluminium, titanium and boron seem to have no obvious effects on the carbide precipitation.

Transmission electron microscopy study proves that the alloy additions do not introduce any new carbide types or changes of the carbide type [28]. Only one carbide phase, $M_{23}C_6$ type carbide, exists in these modified alloys, as observed in the slowly cooled cast base alloy, although the chemical compositions of carbide particles are changed to a certain extent. EDS microanalysis results indicate that the contents of other principal metallic elements are also affected besides the occurrence of nickel in the $M_{23}C_6$ carbide with nickel additions to the base alloy. Molybdenum content in the carbide increases with increasing nickel content in the alloys, but the contents of chromium and cobalt decrease. The additions of aluminium, titanium and boron result in the $M_{23}C_6$ carbide containing a higher molybdenum content with respect to the alloys with the same nickel content level without these trace element additions [28].

Additionally, it is shown in Fig. 1 that the distribution of carbide precipitates is not affected by modifying the base alloy with alloy additions. Carbide particles are observed mainly to have precipitated within the interdendritic regions and almost no grain-boundary carbide precipitation is observed.

Microstructures of the base alloy and the modified alloys are examined by transmission electron microscopy. A decrease in the density of fine crystal defect microstructures, such as dissociated dislocations, stacking faults and twins, with the increase of nickel content in the alloys is demonstrated by transmission electron microscopy observations, as shown in Fig. 2. No such effects caused by the additions of the trace elements are observed in this alloy system. This may be interpreted in terms of the effects of SFE on the formation of these microstructures because nickel additions increase the alloy's SFE significantly [29] and the density and distribution of such crystal defect microstructures as dislocations, stacking faults and twins are known to be associated with the SFE of the alloy.

The results of tensile tests and Vickers microhardness measurements for the base alloy and the modified alloys are shown in Fig. 3. The effects of alloy additions on the transient mechanical properties of this alloy system are more complicated than those caused by the changes in casting conditions of the cast Co–Cr–Mo alloy, which has been discussed in our previous paper [1]. It is shown that the tensile strengths, both tensile yield stress and tensile breaking stress, and microhardness of the alloys decrease while tensile elongation increases with nickel additions to the base alloy. The extent of the changes in these property parameters is increased with the increase of the nickel content in the alloys and this trend is seen much more sharply in the low nickel content region than in the high nickel content region. Alloys with additions of the minor trace elements aluminium, titanium and boron show higher tensile strengths, tensile elongation and hardness than the alloys without the trace element additions containing the same nickel content.

Although the addition of nickel lowers the tensile strengths and hardness of the as-cast Co–Cr–Mo alloys, a tensile yield stress of 451 MPa, a tensile breaking stress of 736 MPa and an HV hardness value of 269 are still obtained even in an alloy containing nickel up to about 9 wt % and without other element additions. These mechanical property parameters can still meet the requirements as given in the standard specification (F 75–82) for this alloy used for surgical implant applications [30]. However, a significant improvement in ductility and fatigue crack growth resistance [31] is achieved by the nickel additions to the base alloy.

The effects of nickel on the transient mechanical properties of alloys are considered to be related to the deformation mechanisms during testing because the alloy's SFE increases with nickel additions. It is well known that the slip deformation process in the fcc

TABLE I Composition of as-cast alloys used in the present study

Alloy no.	Chemical composition (wt %)										
	Cr	Mo	Ni	C	Fe	Si	Mn	Co	Ti	Al	B
1	29.07	6.69	–	0.16	0.06	0.05	0.10	bal.	–	–	–
2	27.59	6.49	4.28	0.15	0.06	0.05	0.09	bal.	–	–	–
3	26.24	6.13	9.03	0.15	0.06	0.05	0.09	bal.	–	–	–
4	28.84	6.35	–	0.16	0.06	0.08	0.10	bal.	0.12	0.11	0.01
5	27.40	6.23	4.50	0.16	0.06	0.08	0.10	bal.	0.11	0.11	0.01
6	25.71	5.98	9.48	0.15	0.05	0.07	0.09	bal.	0.11	0.11	0.01

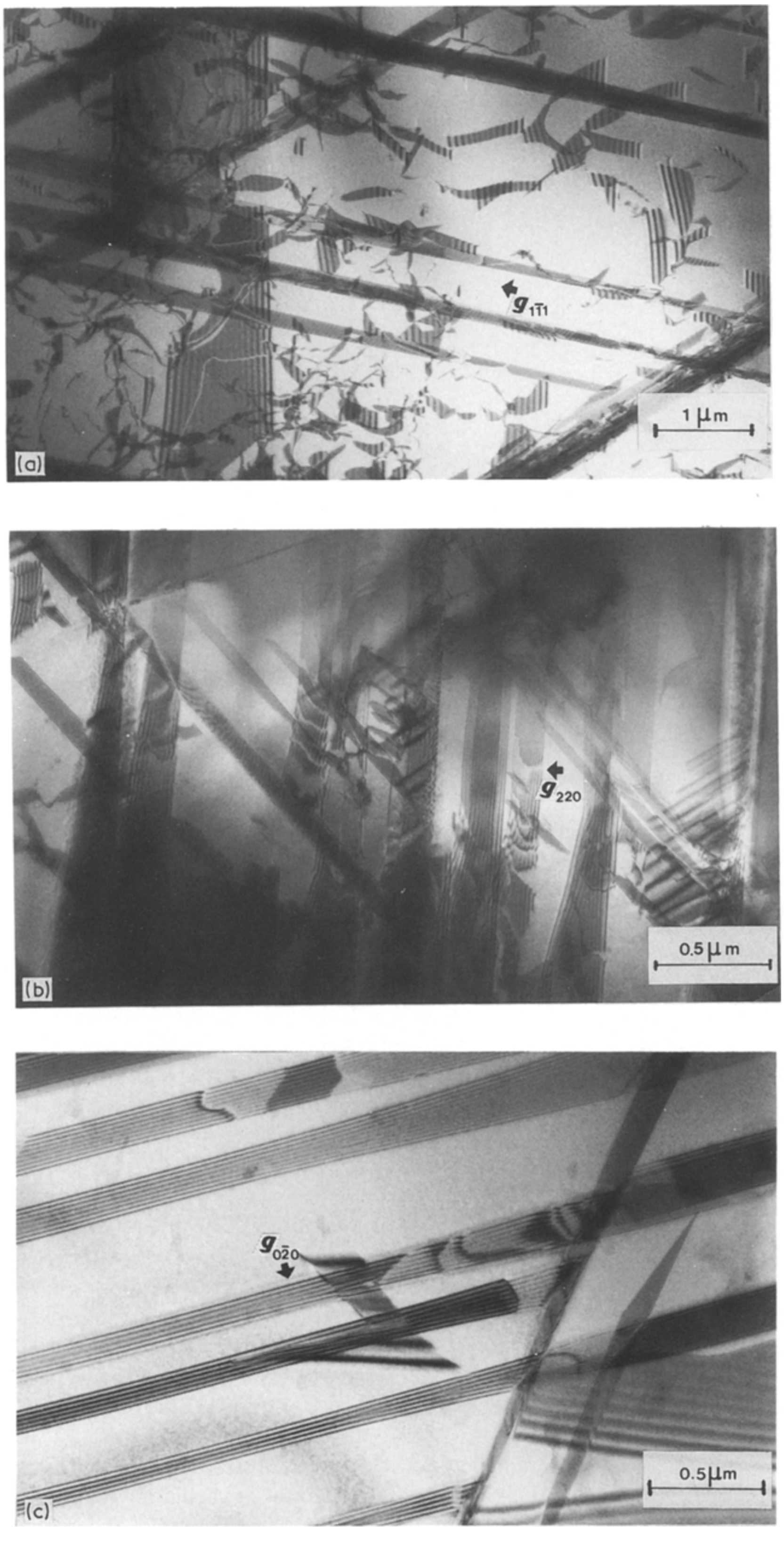

Figure 2 Transmission electron micrographs showing the effects of nickel additions on the structures of dissociated dislocations, stacking faults and twins in the as-cast Co–Cr–Mo alloy. (a) The base alloy, (b) the alloy with 4 wt % nickel, and (c) the alloy with 9 wt % nickel.

phase will be restricted by the presence of stacking faults or twins. As the density of stacking faults and twins increases, the mean free slip path will decrease and a higher strength is to be expected. The addition of nickel to the base alloy decreases the density of dissociated dislocations, stacking faults and twins, thus rationalizing in terms of the f c c slip mechanism the improvement in mechanical properties observed in the present study. On the other hand, the effects of the trace element additions on the transient mechanical properties are mainly attributed to the improvements in casting structure, where microstructural casting defects such as shrinkage porosity, interdendritic segregation, nonmetallic inclusions and even coarse grain size can be minimized by minor additions of aluminium, titanium and boron.

Special interest has been given to the effects of nickel additions on the tensile ductility of the alloys. It is noted in Fig. 3 that a more than doubled tensile elongation value compared to the base alloy are obtained in the alloys with nickel contents about 4 to 4.5 wt % with and without the trace element additions,

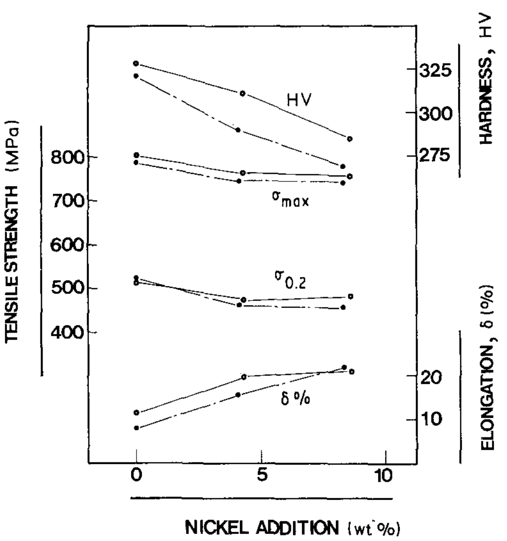

Figure 3 Tensile properties and hardness of the as-cast alloys showing the effects of alloy additions on the mechanical properties in the Co–Cr–Mo alloys. (○) With, (●) without aluminium, titanium or boron.

respectively. However, for the alloys with even higher nickel content, the effects of nickel on the tensile ductility do not seem to be so obvious. A schematic representation of the tensile stress–strain curves for the alloys with or without nickel additions is shown in Fig. 4. For the alloys with no nickel addition, a type-I like stress–strain response as described in the literature [32] is observed. The specimen fractures with almost no homogeneous plastic deformation process. However, for the alloys with nickel additions, a typical type-II stress–strain curve, so called elastic–homogeneous plastic response, is observed. Both an elastic region at small strains and a smooth parabolic portion of the curve, which is associated with homogeneous plastic deformation processes such as the irreversible moment of dislocations, are seen in the tensile curves of the alloys with nickel additions. The difference in the tensile stress–strain curves of these two categories of the alloy is consistent with the macro- and micro-examinations of the alloys' tensile fracture specimens.

Fig. 5 shows side views of the tensile specimens after testing. SEM micro-examination of the tensile fracture surfaces of the alloys is shown in Fig. 6. In Fig. 5, it is seen that alloys 1 and 4 (without nickel

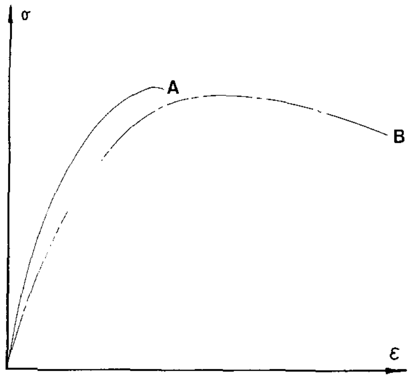

Figure 4 A schematic representation of tensile stress–strain curves showing the difference in the tensile behaviour between the alloys without nickel additions (a) and with nickel additions (b).

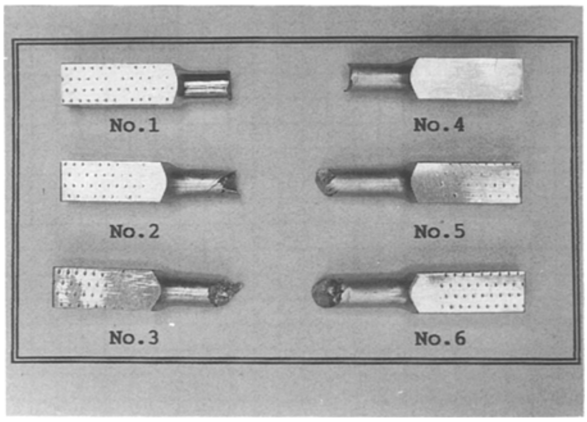

Figure 5 Macroexamination of the side views of the tensile specimens after testing.

additions) exhibit a typical macroscopically brittle fracture feature where the fracture surfaces are flat and perpendicular to the direction of the applied stress, while the alloys with nickel additions exhibit a ductile fracture feature where the fracture surfaces are rather rough showing a large shear-lip zone. The fracture surfaces form an angle of about 45° to the direction of the applied stress, in contrast to the situation in brittle fractures. The scanning electron micrographs of tensile fracture surfaces also indicate significant differences in the fracture appearances between alloys with or without nickel additions. A brittle fracture mode, in which the material fractures between dendrites, is observed in the alloys without nickel additions, as shown in Figs 6a and d. A ductile fracture mode in which the material fractures by tearing with a matte surface is observed in the alloys with high nickel content, as shown in Figs 6c and f. In the alloys with low nickel content, a mixture of the above two fracture modes is seen, as shown in Figs 6b and e.

4. Conclusions

Modifying the composition of the Co–Cr–Mo alloy with additions of nickel and some trace elements such as aluminium, titanium and boron does not seem to result in changes in the nature of the cast structure. A directional, coarse dendritic cast structure is produced in the modified alloys as in the base alloy. A reduction in the grain size of about 5% to 10% is caused by the minor additions of aluminium, titanium and boron. It is found that both the amount and the particle size, and therefore the total amount of carbide precipitates decrease strikingly with the increase of nickel content in the alloys. In addition, the density of dissociated dislocations, stacking faults and twins is observed to decrease with the increase of nickel content because nickel additions to the base alloy increase the alloy's SFE significantly.

Tensile strengths and microhardness of the alloys decrease while tensile elongation increases with nickel additions to the base alloy. Minor additions of the trace elements aluminium, titanium and boron improve the transient mechanical properties, including tensile strengths, hardness and ductility. The effects of nickel on the mechanical properties of the alloys are con-

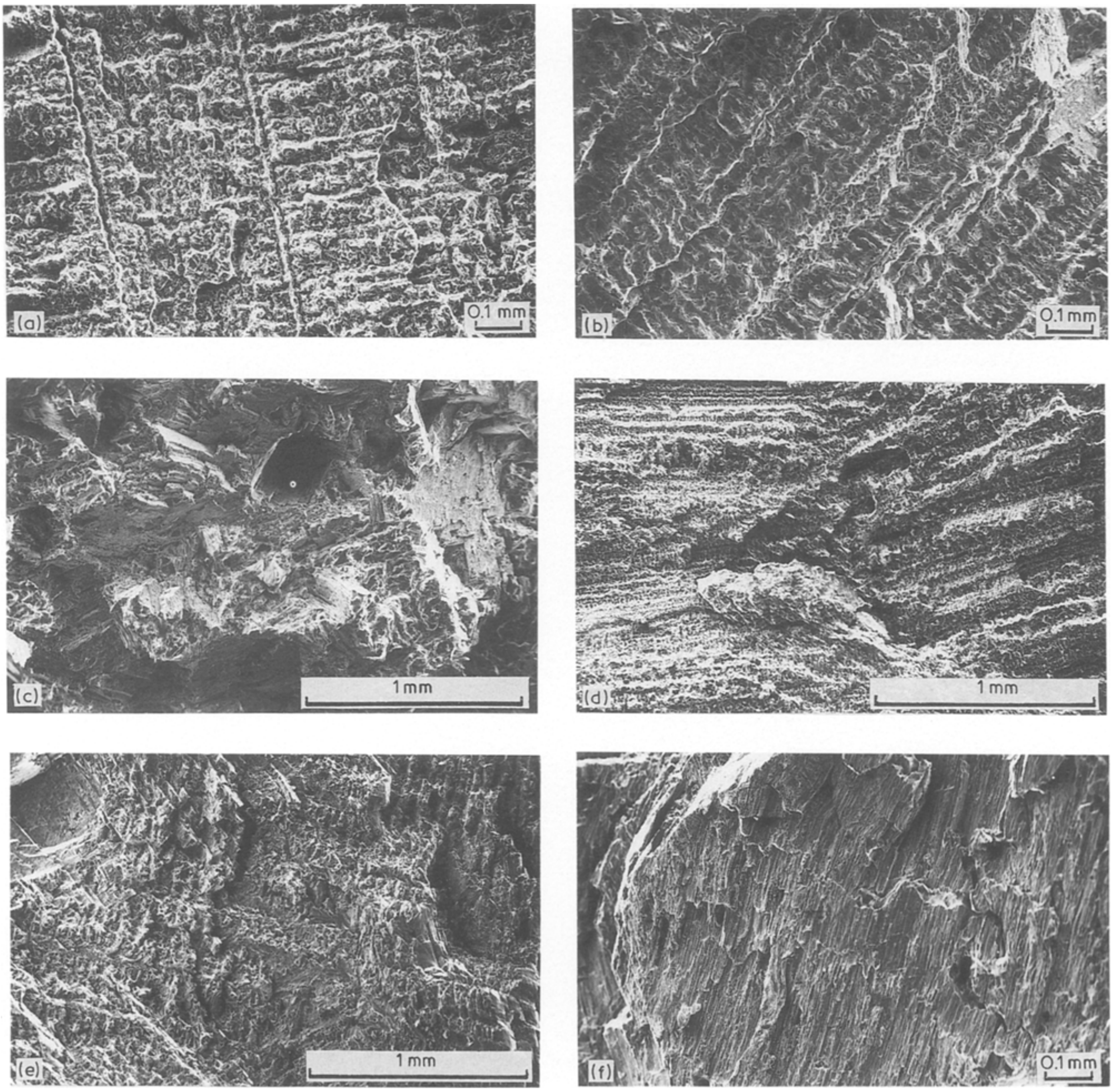

Figure 6 Scanning electron micrographs showing the effects of alloy additions on the tensile fracture appearance of the as-cast alloys, (a) to (f) corresponding to alloys 1 to 6 listed in Table I.

sidered to be related to the deformation mechanisms during testing because of the changes in the alloy's SFE, whereas the effects of the trace element additions on the mechanical properties are mainly attributed to the improvements of the casting structure.

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