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Ductility and Precipitation in Sintered Tungsten Alloys

D. RITTEL and I. ROMAN

Graduate School of Applied Science and Technology, The Hebrew University of Jerusalem, Jerusalem 91904 (Israel)

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ABSTRACT

The effects of post-sintering heat treatments were studied employing two tungsten alloys. For the first alloy, a typical heavy alloy with 90 wt.% W, heat treatments ($T >$ 600 °C) resulted in improved tensile ductility. For the second alloy, the composition of which was similar to that of the matrix phase of a heavy alloy, heat treatments resulted in age hardening as a result of precipitation phenomena, none of which were observed in the matrix of heavy alloys. It was thus concluded that the improved ductility of heat-treated heavy alloys is not caused by precipitation but rather is due to other factors, such as residual interfacial thermal stress relief together with dissolution of embrittling phases and/or elements.

1. INTRODUCTION

High tungsten (greater than 85 wt.%) sintered heavy alloys, having the typical microstructure shown in Fig. 1, consist of spherical b.c.c. tungsten single crystals embedded in an f.c.c. W-Ni-Fe (or W-N-Cu) matrix, the composition of which is typically 25.5W-47Ni-27.5Fe (in approximate weight per cent). These alloys are sintered in reducing atmospheres at temperatures ranging typically from 1420 to 1470 °C, followed by furnace cooling. Their lack of tensile ductility has been attributed to hydrogen embrittlement or to the presence of intermetallic compounds which impair the strength of the tungsten grain-matrix interface (for a detailed discussion see for example ref. 1). This relatively low tensile ductility of the as-sintered alloys is known to be significantly improved by subjecting them to annealing treatments at temperatures above 1000 °C followed by rapid cooling.

Precipitation and aging phenomena which are well documented for numerous alloy systems [2, 3] have been recently reported to exist in (30-40)W-Ni-Fe alloys subjected to various thermal treatments [1]. Furthermore, it has been proposed [4] that aging and precipitation phenomena occurring in the matrix are responsible for the improvement in ductility, although no precipitation could be detected and identified in the matrix of heavy alloys [5]. It has also been reported that low temperature (600 °C) annealing treatments result in a similar increase in the ductility as observed for the higher temperature treatments [6, 7].

In order to clarify whether precipitation plays a role in the improvement of ductility, we examined both a heavy alloy and another alloy, similar in composition to that of the matrix phase of the heavy alloy, both of which are subjected to similar annealing treatments.

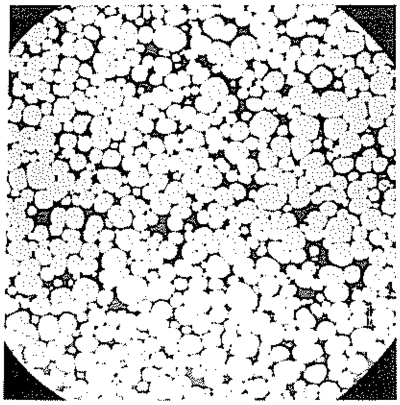

Fig. 1. Typical microstructure of as-sintered material (etchant, mixed acids). (Magnification, 120×.)

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2 MATERIALS AND EXPERIMENTAL PROCEDURE

90W-7Ni-3Fe alloy was sintered at 1470 °C and allowed to furnace cool, according to reported procedures [8]. Tensile and impact specimens were machined and subjected to annealing treatments for 3 h at different temperatures (Table 1), followed by an oil quench. The heat treatment of all the samples was carried out in our laboratory in a commercial hydrogen-free nitrogen protective atmosphere [8] in order to minimize the possibility of hydrogen embrittlement. The matrix-like alloy (of composition 25.5W-47Ni-27.5Fe) was sintered and cooled in the same conditions. This alloy was subjected to two different types of thermal treatment, namely (1) isochronal (3 h) annealing treatments, at different temperatures, identical with those utilized for the heavy alloy (Table 1) and (2) isothermal (1000 °C) treatments for different times (Table 2). The compositions were determined using a carefully calibrated energy-dispersive X-ray analysis technique. In certain cases a fully quantitative analysis was not possible because of instrumental restrictions. These cases will be referred to as "qualitative analysis".

TABLE 1

Summary of isochronal (3 h) thermal treatments

Temperature (°C)	*Matrix alloy*	*Heavy alloy*
Untreated	*	*
300		*
400		*
500	*	*
600		*
700	*	*
800		*
900	*	*
1000		*
1100	*	*

*, thermal treatment carried out in these cases.

TABLE 2

Summary of isothermal treatments applied to the matrix alloy

Temperature (°C)	*Time* (h)
1000	1.5
1000	3
1000	24
1000	50

3 RESULTS

3.1. *Heavy alloy*

3.1.1. *Mechanical and impact properties*

The variation in mechanical properties of the heavy alloy subjected to annealing treatments is shown in Fig. 2. From these figures, it appears that isochronal heat treatments starting at relatively low temperatures (500-600 °C) result in increased tensile ductility and strength, whereas impact properties show little improvement (Fig. 3).

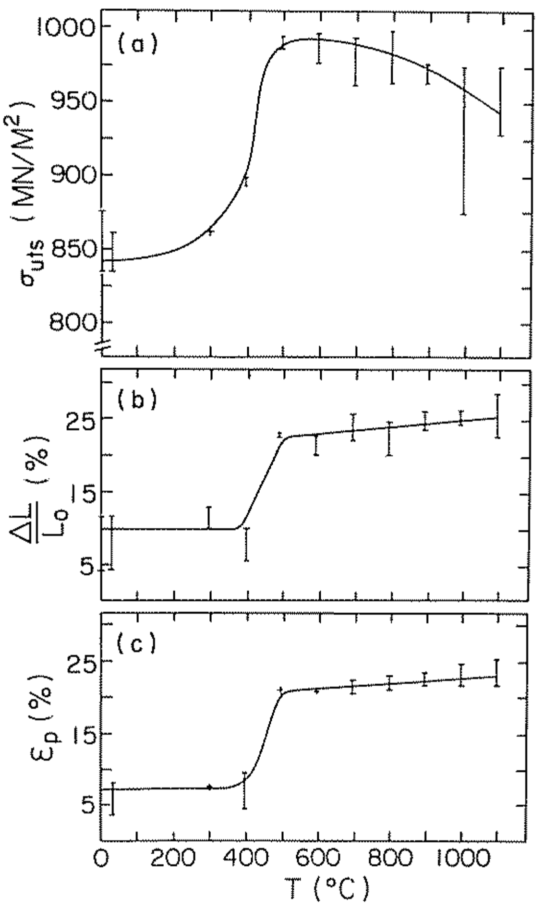

Fig. 2. Mechanical properties ((a) ultimate tensile strength, (b) tensile elongation and (c) plastic strain) of the heavy alloy *vs.* treatment temperature.

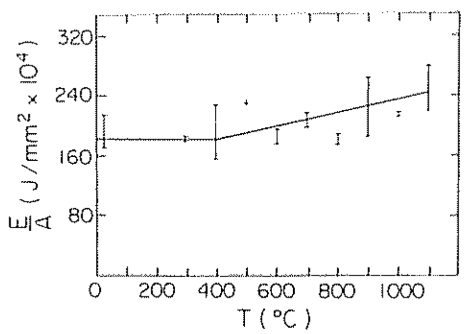

Fig. 3. Impact energy of the heavy alloy *vs.* treatment temperature.

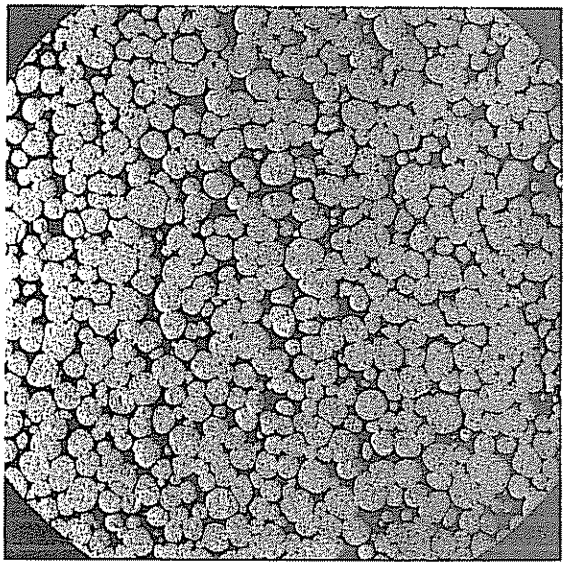

Fig. 4. Typical microstructure of annealed material (etchant, mixed acids). (Magnification 170×.)

3.1.2. Metallography

A typical micrograph of the annealed alloy is shown in Fig. 4. No noticeable changes in the morphology of the alloy occur as a result of the annealing treatment. A typical tungsten grain size is 40 μm and a typical matrix mean free path is of the order of magnitude of 10 μm. No grain boundaries in the matrix are discernible nor is any type of precipitation.

3.1.3. Fractography

Extensive fractographic studies of the fracture surfaces of broken heavy alloy samples were conducted, and it was noted that the increased ductility after heat treatment is characterized by transgranular cleavage of the tungsten grains. This is in contrast with the

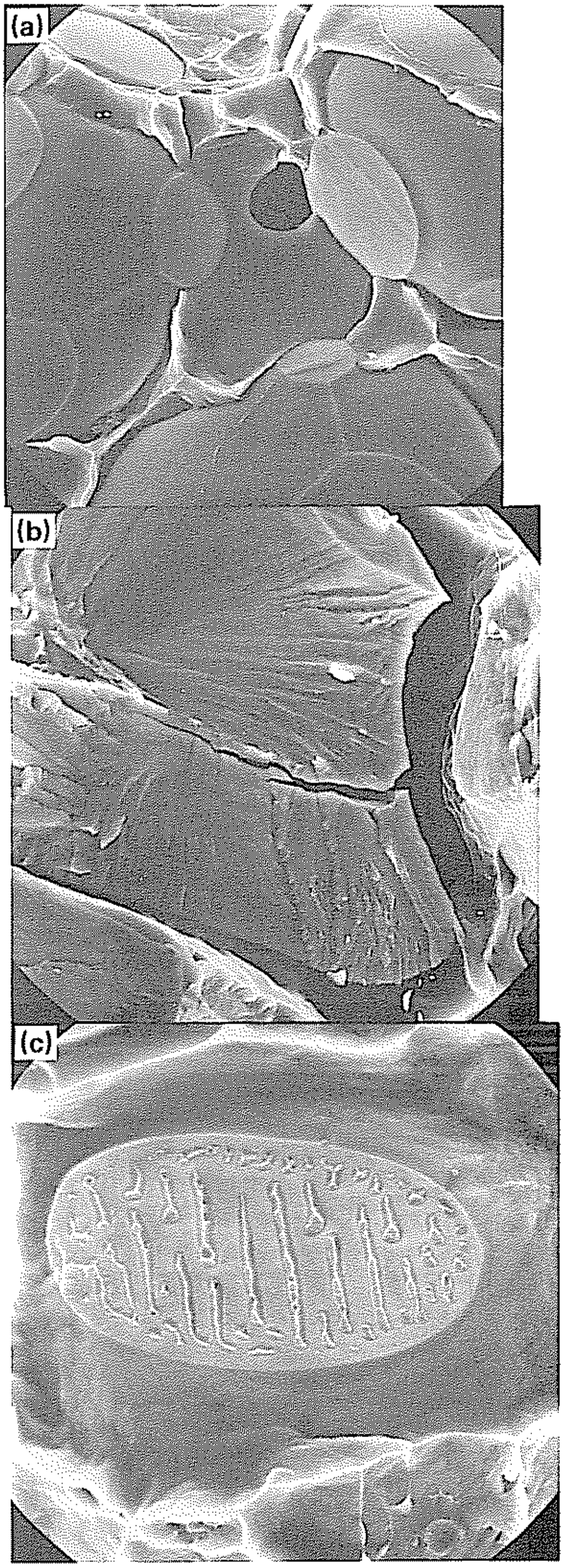

Fig. 5. (a) Scanning electron fractograph of tungsten grain separation (untreated heavy alloy); (b) scanning electron fractograph of a cleaved tungsten grain (treated heavy alloy); (c) scanning electron fractograph of precipitation on a tungsten binding neck. (Magnifications: (a) 3250×; (b) 5500×; (c) 4500×.)

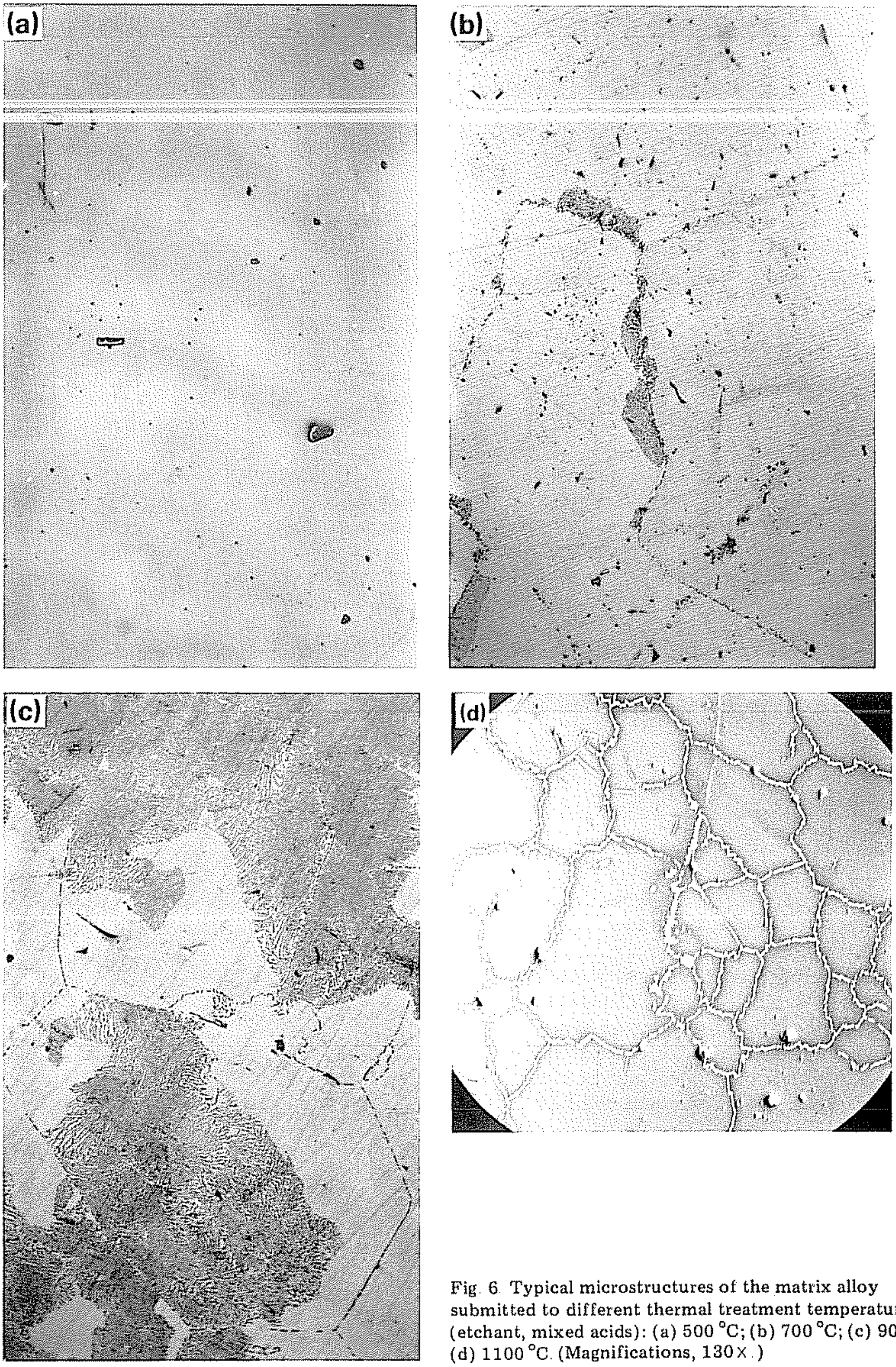

Fig. 6. Typical microstructures of the matrix alloy submitted to different thermal treatment temperatures (etchant, mixed acids): (a) 500 °C; (b) 700 °C; (c) 900 °C; (d) 1100 °C. (Magnifications, 130×.)

as-sintered alloy which fails in an intergranular mode (Figs. 5(a) and 5(b)).

One interesting feature observed is the occurrence of highly geometrical ordered precipitates on the tungsten linking necks, which appear when annealing temperaures are higher than 700-800 °C (Fig. 5(c)).

3.2. *Matrix alloy*

3.2.1. *Effects of annealing temperature*

Typical microstructures of the matrix alloy after annealing at various temperatures are shown in Fig. 6.

Annealing temperatures of up to 500 °C produce homogenization of the microstructure, in the sense that no grain boundaries are discernible and no noticeable precipitation is observed.

Annealing at 700 °C results in a continuous precipitation outline of the grain boundaries and, in addition, some discontinuous lamellar precipitation originating at grain boundaries becomes noticeable, although individual lamellae are poorly resolved. A typical grain size was found to be in the range 20-50 μm. Elevating the annealing temperature to 900 °C increases the amount of discontinuous precipitation and individual lamellae become readily resolved. Grain boundaries are now better defined and are outlined by localized precipitation. When the annealing temperature is increased to 1100 °C, the phenomenon is reversed; discontinuous precipitated phase dissolves in the parent material whereas grain boundary precipitation remains unaffected.

The variation in the microhardness (with annealing temperature) is summarized in Fig. 7. When discontinuous precipitation was present, the microhardness was also measured in the precipitated phase.

The tungsten concentration in the various phases produced was determined by energy-dispersive X-ray analysis and it was found that the parent phase contains about 26 wt.% W whereas the continuous phase along the grain boundaries contains about 77 wt.% W (determined for the sample annealed at 1100 °C). This allows tentative identification of the precipitate as the W-Ni intermetallic compound of the binary phase diagram or the W(N, Fe) phase of the ternary system [9].

Qualitative analysis of the lamellar precipitation indicated a high tungsten content; however, experimental limitations did not allow a more precise determination of the composition of the lamellae.

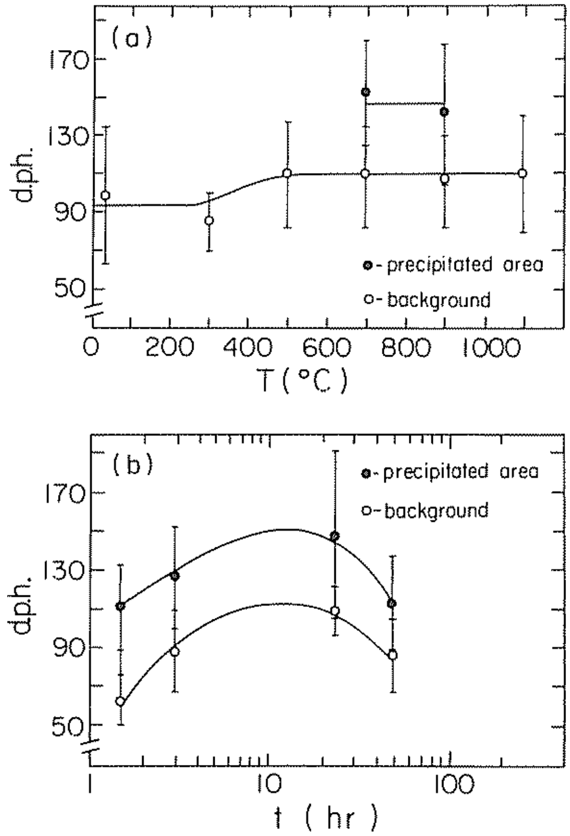

Fig. 7. The microhardness (*i.e.* the diamond pyramid hardness d.p.h.) of the matrix alloy (a) *vs.* treatment temperature and (b) for the isothermal treatment: ●, precipitated area; ○, background.

The discontinuous precipitation process is accompanied by tungsten depletion of the parent phase from an initial 26 wt.% W to less than 20 wt.% W at 1000 °C. Dissolution of the discontinuous precipitation at 1100 °C restores the original tungsten content.

3.2.2. *Effect of annealing time at 1000 °C*

Typical microstructures resulting from annealing treatments at 1000 °C for up to 50 h are shown in Fig. 8. As expected, the phenomena observed are similar to those described above, *i.e.* continuous precipitation which outlines the grain boundaries together with lamellar-type discontinuous precipitation within the grains.

The area fraction covered by the lamellar precipitates increases exponentially with an-

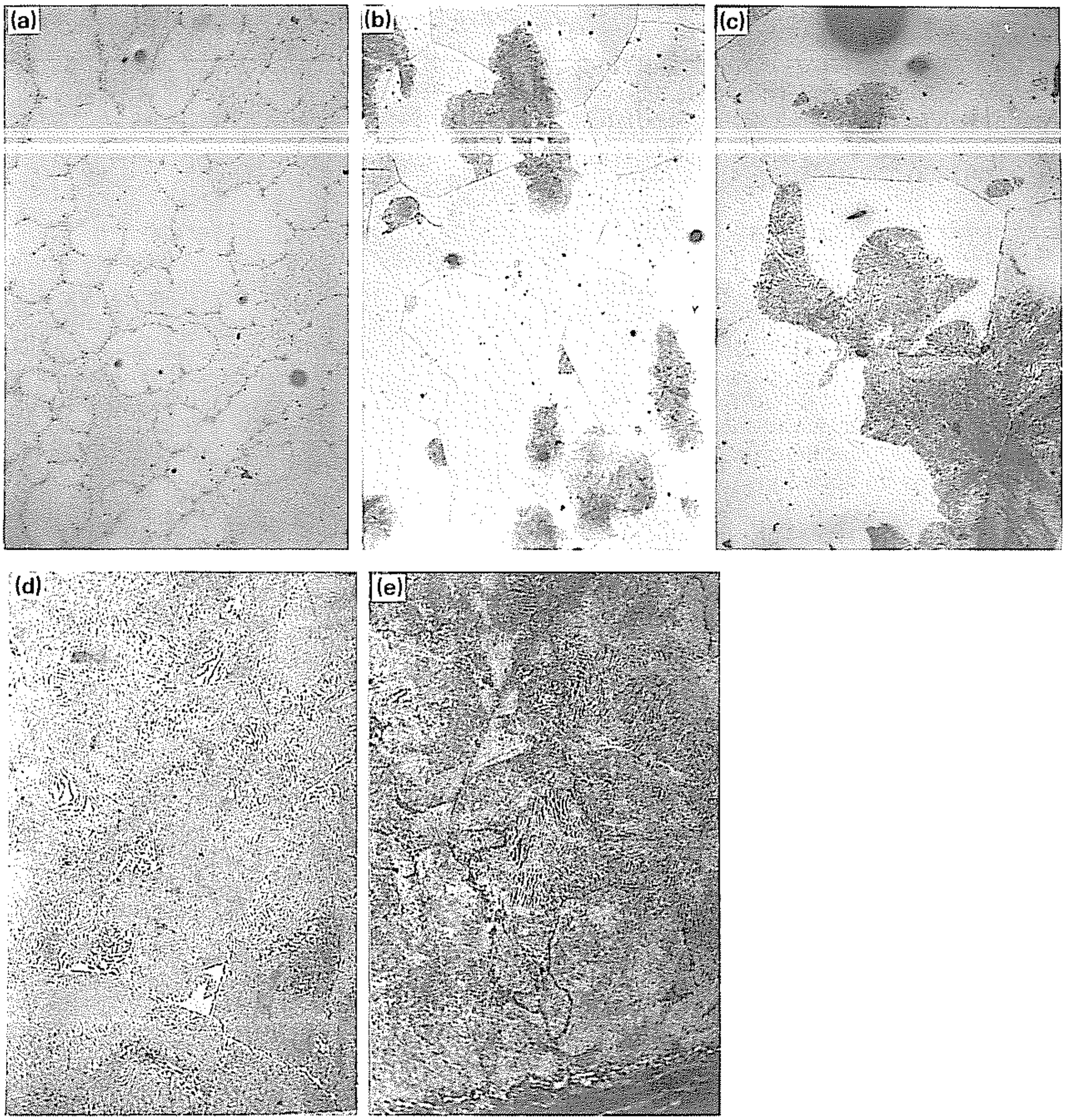

Fig. 8. Typical microstructures of the matrix alloy submitted to different isothermal treatments (etchant, mixed acids): (a) untreated; (b) 1.5 h; (c) 3 h; (d) 24 h; (e) 50 h. (Magnifications: (a), (b) 50×; (c)–(e) 100×.)

nealing time and reaches saturation at about 24 h. The precipitates appear to be stable and no spheroidization or dissolution was noticed even after annealing for 50 h. The variation in microhardness with annealing time is summarized in Fig. 7. Energy-dispersive X-ray analysis performed on the background material again indicates increased tungsten depletion with annealing time.

4 DISCUSSION

An alloy, the composition of which is similar to the matrix of heavy alloys, was subjected to various annealing treatments in order to study their effects on metallurgical properties of the matrix.

The experimental results indicate that annealing treatments at temperatures in excess of 700 °C result in precipitation phenomena of two types, namely (1) continuous grain boundary precipitation and (2) discontinuous lamellar precipitation originating at grain boundaries. The grain boundary precipitates were tentatively identified as a W(Ni, Fe) ternary compound or a W–Ni binary compound, according to their composition. The lamellar precipitation was found to have a high tungsten content and has been reported [1] to be made of pure tungsten.

Identification of the NiW grain boundary precipitate is supported by the fact that, while lamellae dissolved at an annealing temperature of 1100 °C, the grain boundary precipitate is still present as expected from the phase diagram of the NiW compound [9].

The precipitation phenomena described above are not readily observed in the matrix of heavy alloys subjected to similar annealing treatments. Furthermore, hardness measurements indicate that peak aging in the matrix alloy is achieved after treatment at 1000 °C for about 15 h, whereas changes in the mechanical properties of the annealed heavy alloy are obtained after exposure to lower temperatures and/or shorter times.

These differences can be explained if it is realized that the subject matrix alloy is polycrystalline with a typical grain size range 20–50 μm, whereas in heavy alloys the matrix mean free path (between the tungsten spheres) does not exceed 10 μm and no grain boundaries are observed. Such a short mean free path suggests that precipitation phenomena are likely to be located on the tungsten grains themselves.

Another important difference between the matrix alloy and the heavy alloy is that high tungsten concentration gradients exist in the heavy alloy because of the presence of pure tungsten grains, whereas no such gradients are present in the matrix alloy.

Consequently, it is not surprising that the fractographic features typical of annealed heavy alloys indicate that some precipitation (on a much finer scale) occurs on the boundaries of tungsten grains. This requires flux against the concentration gradient, which is possible in ternary alloys because of the reduction in the chemical potential [10].

In view of these dissimilarities between the precipitation characteristics of the matrix of heavy alloys and those of the matrix alloy discussed, it is unlikely that the precipitation phenomena which harden the matrix alloy are responsible for the improvement in the mechanical properties of heavy alloys on post-sintering annealing. Rather, it seems that the operation of a combination of other mechanisms such as residual interfacial thermal stress relief [11] and dissolution of embrittling phases or elements [12, 13] causes the observed improvement.

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