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Microstructures and mechanical properties of boride-dispersed precipitation-hardening stainless steels produced by RST

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Two commercial precipitation-hardening (PH) stainless steels were modified with 2.64 to 2.86 wt% Ti and 1.2 to 1.3 wt% B via rapid solidification technology (RST) and powder metallurgy (PM). The resulting alloys exhibited improved tensile and yield strengths over their commercial PH stainless steel counterparts at room and elevated temperatures. Ductility improvements at elevated temperatures were also observed. The improved mechanical properties were due to extremely fine microstructures stabilized by a fine dispersion of boride phases.

1. Introduction

During the last twenty years, the progress in rapid solidification technology produced a host of new alloys of novel compositions and microstructures. These new alloys exhibited improvements in mechanical properties, magnetic properties, and/or corrosion resistance [1–5].

In a recent communication [6], we reported our investigation of a commercial PH 15-7 Mo PH stainless steel modified with 2.1 wt % boron. The alloy, designated Markomet 1120, was produced by a combination of RST and PM. The alloy exhibited improved mechanical properties at an elevated temperature (811 K) via generation of an ultrafine-grained microstructure stabilized by boride phases.

In the continued alloy development activity at Marko Materials, an effort was underaken to further enhance the mechanical properties of the commercial PH stainless steels primarily by modification of their compositions. The present paper reports the results of our study on the mechanical properties and microstructures of two such alloys.

Two new alloys, designated Markomet 1480 and Markomet 1483, were obtained by modifying two commercial PH stainless steels with titanium and boron. Markomet 1480 was based on commerical PH 13-8 Mo stainless steel, while Markomet 1483 was based on commercial Custom 450 PH stainless steel. The nominal compositions of these two RST alloys and the two corresponding commerical PH stainless steels are given in Table I.

As second iteration alloys to Markomet 1120 [6], Markomet 1480 and Markomet 1483 contained significantly less boron than Markomet 1120 (1.2 to 1.3 compared to 2.1 wt % B). An additional element, titanium, was added to these alloys because titanium is a strong boride former. It was hoped that boron would precipitate out mostly as titanium borides and leave the matrix composition similar to that of the base PH steels. If this happened, the alloys would respond to the standard heat-treatment procedures established for commercial PH stainless steels. Titanium and boron were added to the steels in stoichiometric proportions to allow a preferential formation of stable titanium diborides. An important difference to note in composition was that Markomet 1120 had 2.2 wt % Mo, Markomet 1480 contained 2.5 wt % Mo, and Markomet 1483 contained only 0.8 wt % Mo.

2. Experimental procedure

Markomet 1480 and Markomet 1483 were initially prepared as rapidly solidified ribbons by melt spinning at a cooling rate of 10^6 K sec^{-1} [7]. The ribbons were pulverized into powders of desirable sizes by a rotating hammer mill. The powders were consolidated into fully dense bars by hot extrusion. Extruded bars were isothermally aged between 700 K (800° F) and 811 K (1000° F) from 1 to 360 h in air, followed by air cooling to room temperature.

The ultimate tensile strength, 0.2% offset yield strength, and per cent elongation of Markomet 1480 aged at 811 K (1000° F) and Markomet 1483 aged at 783 K (950° F) were tested at temperatures from room temperature to 839 K (1050° F).

The microstructural characteristics of Markomet 1480 and Markomet 1483 both aged at 773 K (930° F) for 7 h were investigated by optical and scanning electron microscopy (SEM). The various precipitate phases were qualitatively analysed and identified by energy dispersive X-ray analysis (EDX).

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TABLE I Nominal chemistry of Markomet 1480, Markomet 1483, and their commercial PH stainless steel counterparts

Alloy	Composition (wt %)									
	C	Cr	Ni	Mo	Al	Cu	Nb	B	Ti	Fe
Markomet 1480	0.05	13.0	8.5	2.5	1.2	–	–	1.2	2.64	Bal.
PH 13-8 Mo	0.05	13.0	8.5	2.5	1.2	–	–	–	–	Bal.
Markomet 1483	0.05	15.0	6.0	0.8	–	1.5	0.27	1.3	2.86	Bal.
Custom 450	0.05	15.0	6.0	0.8	–	1.5	0.27	–	–	Bal.

3. Results and discussion

3.1. Mechanical properties

The tensile properties of Markomet 1480 aged at 811 K are shown in Figs 1 to 3. The corresponding properties of Markomet 1483 aged at 783 K (950° F) are plotted in Figs 4 to 6. In the same figures, properties of the corresponding commercial PH stainless steels are shown for comparison.

Markomet 1480 had 20 to 25% higher tensile and yield strengths (Figs 1 and 2) than commercial PH 13-8 Mo stainless steel at temperatures from room temperature to 811 K (1000° F). Its ductility (Fig. 3) at room temperature was significantly lower (50%) than that of PH 13-8 Mo. However, at 811 K Markomet 1480 had 10% more ductility than PH 13-8 Mo.

Similarly, Markomet 1483 exhibited improved mechanical properties compared to Custom 450 when tested at temperatures between room temperature and 839 K (1050° F). Its tensile and yield strengths (Figs 4 and 5) showed as much as 35% improvement over Custom 450 at an elevated temperature (839 K). The ductility of Markomet 1483 (Fig. 6) at room temperature was lower than that of Custom 450. However, above 589 K (600° F) 25 to 50% greater ductility than Custom 450 was observed.

The ultimate tensile strength and yield strength of Markomet 1480 were higher than those of Markomet 1483 because the two base commercial PH stainless steels belong to two different groups on the basis of strength. PH 13-8 Mo stainless steel, which was modified to make Markomet 1480, belongs to group 2 (higher strength), while Custom 450, the base steel for Markomet 1483, belongs to group 1 (lower strength) [8]. However, the relative per cent improvements in the tensile properties of Markomet 1480 and Markomet 1483 over their commercial PH stainless steel counterparts were similar for both.

3.2. Microstructures

Markomet 1480 aged at 773 K for 7 h had a very fine and uniform microstructure as seen in an optical micrograph (Fig. 7). Shown in Fig. 8 are a pair of scanning electron photomicrographs consisting of a secondary electron image (SEI) (Fig. 8a) and a back-scattered electron image (BEI) (Fig 8b) of the same area of the sample. These photomicrographs revealed several dispersed phases of different particle sizes. EDX analyses identified five phases as follows:

1. A chromium-rich phase (presumably Cr_2B) having an average particle size of about 1 μm (marked A in Fig. 8b).
2. A (molybdenum, chromium)-rich phase having a particle size of 0.3 to 0.5 μm (marked B in Fig. 8b).
3. A (titanium, molybdenum)-rich phase having an average particle size of 0.2 μm uniformly dispersed (marked C in Fig. 8b).
4. A fine molybdenum-rich phase having an average particle size of 0.1 μm (marked D in Fig. 8b).
5. An extremely fine titanium-rich phase (presumably TiB_2) having a particle size of 0.1 μm or less (marked E in Fig. 8a).

The molybdenum-rich (D) and titanium-rich (E) precipitate phases were difficult to distinguish from SEI (Fig. 8a) alone because of their similarity in particle size. However, they were clearly separated in BEI (Fig. 8b) as particles of light (molybdenum) and dark (titanium) contrast arising from the atomic number difference. The molybdenum-rich precipitates

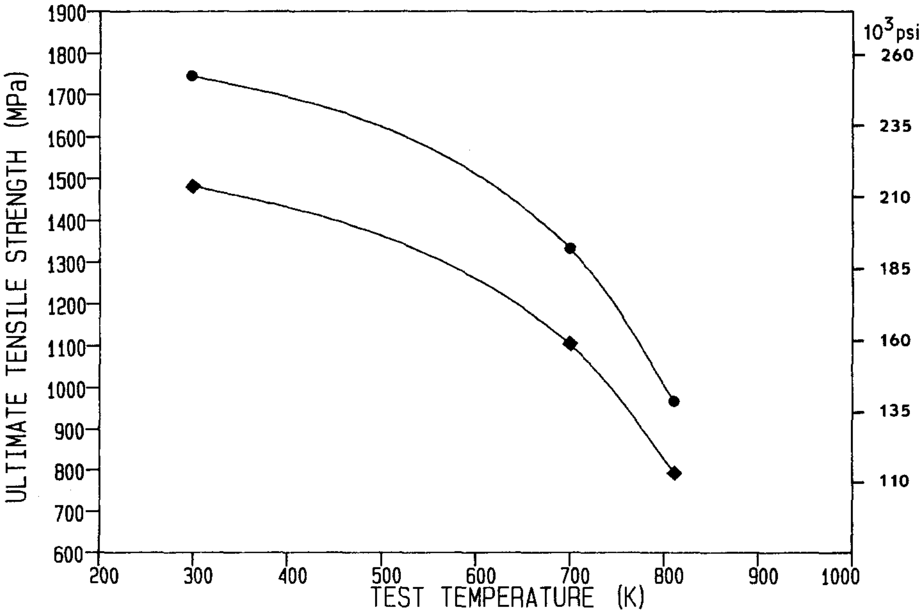


Figure 1 Ultimate tensile strength of (●) Markomet 1480 and (◆) PH 13-8 Mo aged at 811 K (1000° F) as a function of test temperature.

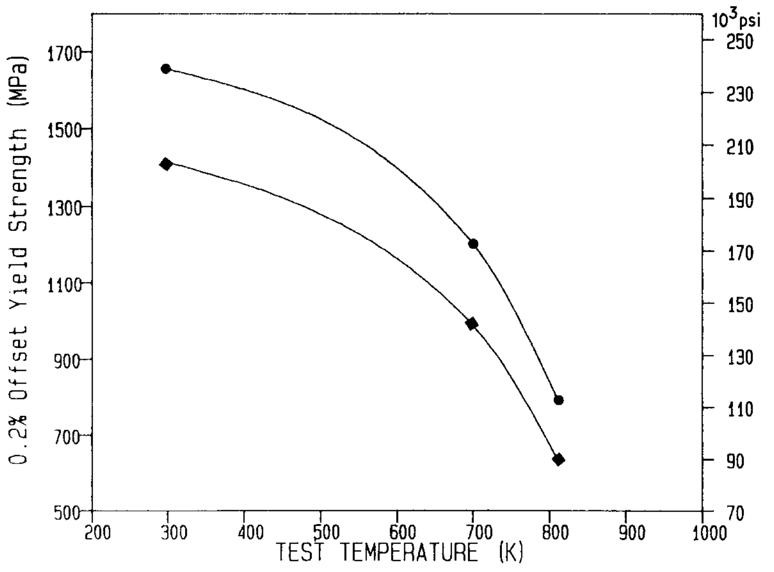
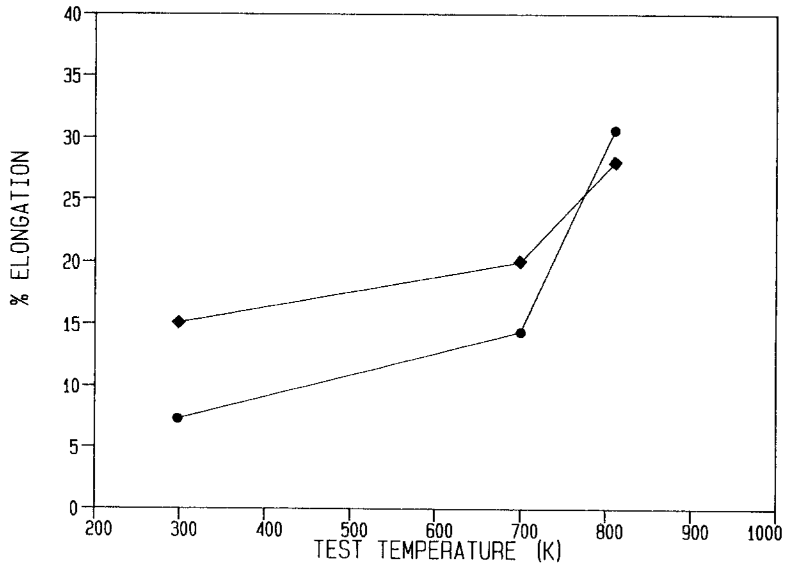


Figure 2 0.2% offset yield strength of (●) Markomet 1480 and (◆) PH 13-8 Mo aged at 811 K (1000 F) as a function of test temperature.

Figure 3 Ductility of (●) Markomet 1480 and (◆) PH 13-8 Mo aged at 811 K (1000° F) as a function of test temperature.



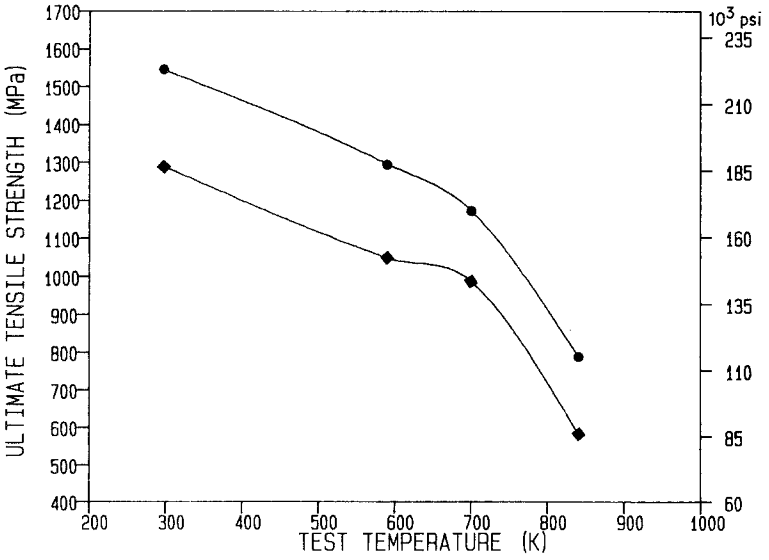


Figure 4 Ultimate tensile strength of (●) Markomet 1483 and (◆) Custom 450 aged at 783 K (950° F) as a function of test temperature.

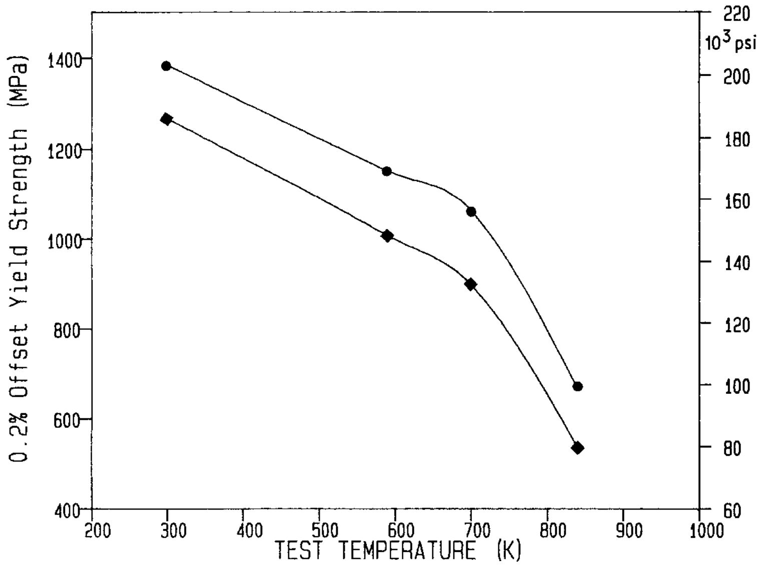
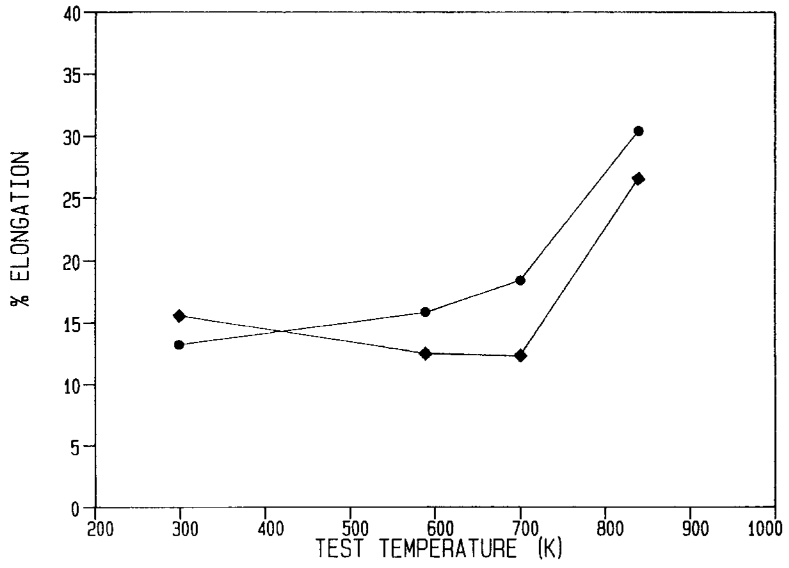


Figure 5 0.2% offset yield strength of (●) Markomet 1483 and (◆) Custom 450 aged at 783 K (950° F) as a function of test temperature.

Figure 6 Ductility of (●) Markomet 1483 and (◆) Custom 450 aged at 783 K (950° F) as a function of test temperature.



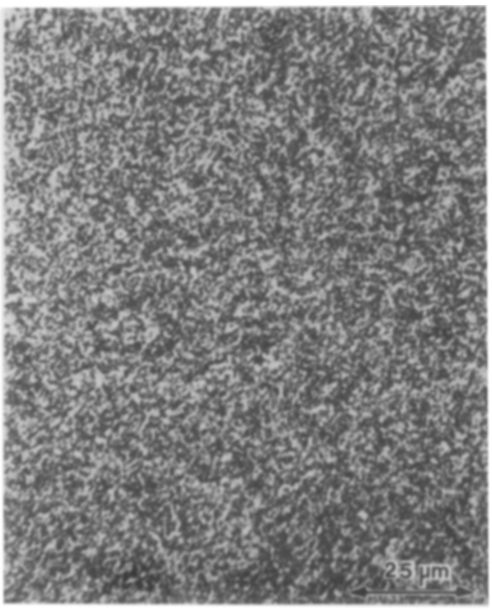


Figure 7 Optical photomicrograph of Markomet 1480 aged at 773 K. Specimen etched in Vilella's reagent.

were seen as fine particles in both SEI and BEI, but titanium-rich particles were seen clearly only in SEI.

These five precipitates were presumed to be borides because boron has negligible solid solubility in steels. Goldschmidt [9] reported that precipitation of M_2B-type borides occurred above 58 p.p.m. in commercial Fe–Cr–Ni-base stainless steels. Wood and Honeycombe [10] achieved 0.1% B in supersaturated metastable Fe–Cr–Ni-base solid solution by rapid solidification. Upon ageing it at high temperatures, he found complex $M_{23}B_6$-type borides precipitated along the grain boundaries. Our earlier investigation of Markomet 1120 showed that the addition of 2.1 % boron to a commercial PH 15-7 Mo stainless steel produced chromium-rich (0.5 to 1.5 μm) and molybdenum-rich (0.1 to 0.3 μm) borides along the grain boundaries when hot consolidated.

Three out of five borides precipitated in Markomet 1480 contained molybdenum. We suspect the alloy was supersaturated with molybdenum, and the supersaturation of molybdenum in metastable solid solution could have provided a high driving force causing

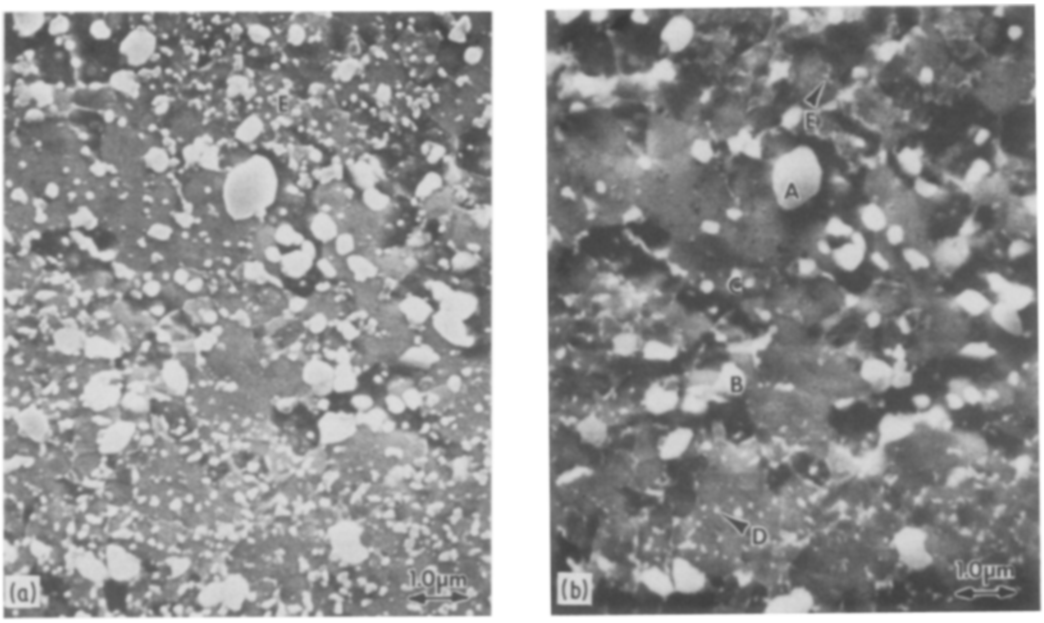


Figure 8 (a) SEI (secondary electron image) and (b) BEI (back-scattered electron image) scanning electron photomicrographs of Markomet 1480 aged at 773 K. (A) Chromium-rich; (B) (molybdenum, chromium)-rich; (C) (titanium molybdenum)-rich; (D) molybdenum-rich; (E) titanium-rich borides.

a copious nucleation and growth of fine molybdenum-containing borides during hot consolidation.

A careful examination of the SEI of Markomet 1480 at high magnification (Fig. 9a) showed that the large chromium-rich and medium size (chromium, molybdenum)-rich borides formed primarily at the grain boundaries. The finer molybdenum-rich and titanium-rich borides formed both along the grain boundaries and inside the grains.

The Markomet 1480 aged at 773 K had a very uniform dispersion of ultrafine precipitates (20 to 30 nm) within the grains as seen in high-magnification SEI micrographs (Figs. 9a and b). These intragranular precipitates are most likely Ni–Al-, Ni–Mo-type intermetallic phases which normally occur in aged conventional PH stainless steels. These ultrafine intermetallic precipitates were also found in Markomet 1120 aged at 773 K [6].

Markomet 1483 aged at 773 K for 7 h, which contained significantly less molybdenum (0.8 wt %) than Markomet 1480 (2.5%), had an extremely fine microstructure as seen in an optical micrograph (Fig. 10). Scanning electron photomicrographs (SEI and BEI) of the same sample (Figs. 11a and b) revealed three different boride precipitates:

1. a large chromium-rich boride phase (presumably Cr_2B) with a particle size between 0.5 and 1.0 μm (marked A in Fig. 11b);
2. a small (titanium, chromium, molybdenum)-rich boride phase with a particle size between 0.3 and 0.4 μm (marked B in Fig. 11b);
3. an extremely fine titanium-rich boride phase (presumably TiB_2) with a particle size between 0.05 and 0.1 μm (marked C in Fig. 11a).

The large chromium-rich borides occurred predominantly at the grain-boundary junctions, while small

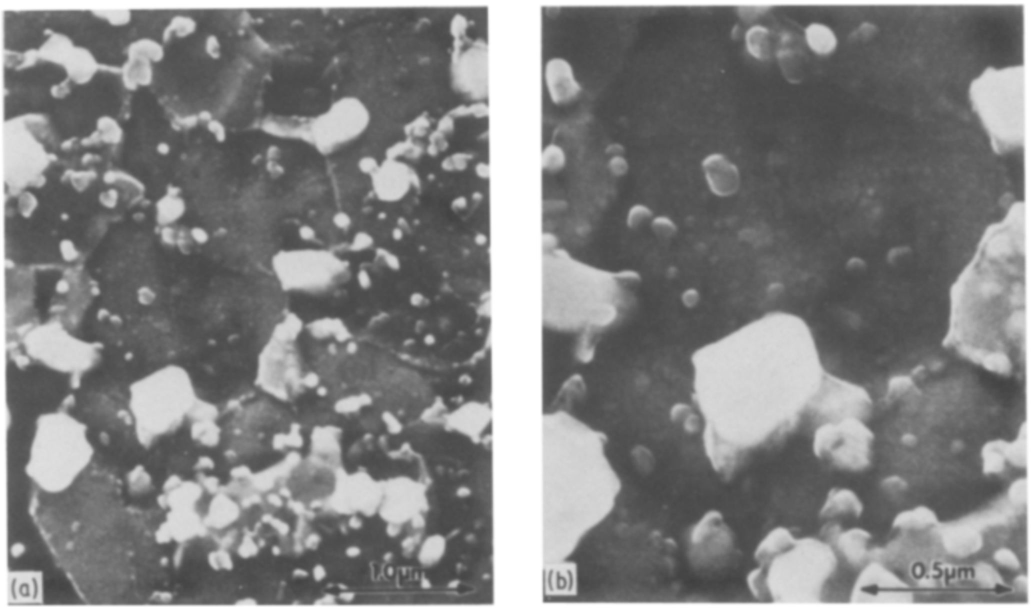


Figure 9 (a), (b) High-magnification scanning electron (SEI) photomicrographs of Markomet 1480 aged at 773 K.

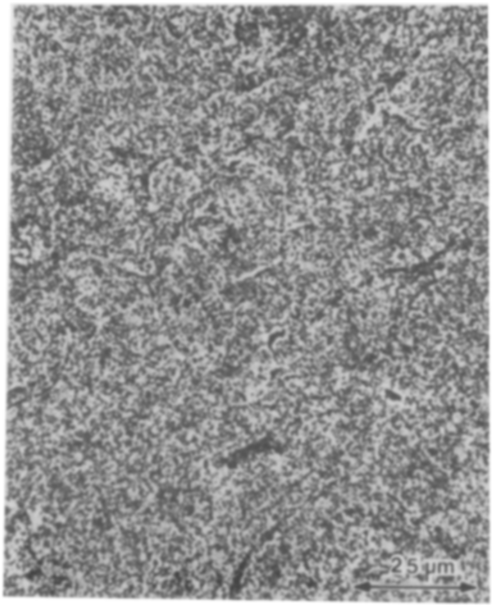


Figure 10 Optical photomicrograph of Markomet 1483 aged at 773 K. Specimen etched in Vilella's reagent.

titanium-rich borides formed along the grain boundaries as well as inside the grains. The number of large chromium-rich borides found in Markomet 1483 and Markomet 1480 was far less than Markomet 1120 [6]. The amount of ultrafine titanium-rich borides precipitated in Markomet 1483 (Figs 11a and b) was much more than Markomet 1480 (Figs 8a and b).

High magnification scanning electron photomicrographs (Figs 12a and b) of Markomet 1483 aged at 773 K for 7 h showed a very uniform dispersion of extremely fine precipitates (20 to 30 nm) within the grain boundaries. These ultrafine intragranular precipitates are presumably of Ni–Mo-, Ni–Cu-, Ni–Nb-types formed during the ageing treatment.

In our earlier study of Markomet 1120 [6] we found the matrix highly depleted in chromium. However, the matrices of both Markomet 1480 and Markomet 1483 were only slightly depleted in chromium. Markomet 1480 had 12.4% Cr in the matrix compared to 13.0% in PH 13-8 Mo stainless steel, while the matrix of Markomet 1483 contained 14.8% Cr compared to 15.0% Cr in Custom 450 stainless steel. As mentioned earlier, these two second iteration alloys contained titanium, a strong boride former, and much less boron than Markomet 1120. As expected, titanium-rich borides formed leaving chromium mostly in the matrix. Furthermore, the addition of titanium and boron to a base PH steel, i.e. Custom 450, which had significantly less molybdenum (0.8%) resulted in a preferential formation and a uniform dispersion of ultrafine and stable titanium-rich borides in Markomet 1483.

4. Conclusions

Markomet 1480 and Markomet 1483 both showed improvements in tensile and yield strengths at room and elevated temperatures when compared to the commercial PH stainless steel counterparts. The improvements in tensile properties of these alloys were mainly due to the refined microstructures obtained by RST. The ultrafine-grained microstructures were stabilized by finely dispersed boride phases.

Five boride phases in Markomet 1480 and three boride phases in Markomet 1483 were found. Both alloys contained titanium-rich borides and a lesser amount of large chromium-rich borides compared to Markomet 1120. The homogeneous dispersion of extremely fine and stable titanium-rich borides in these alloys resulted in ductility improvement at elevated temperatures.

The matrices of Markomet 1480 and Markomet 1483 were only slightly depleted in chromium as a result of titanium addition and reduced boron content.

The principles of RST, combined with a novel alloy design approach, have been successfully applied to produce alloys with improved mechanical properties from commercial PH stainless steels.

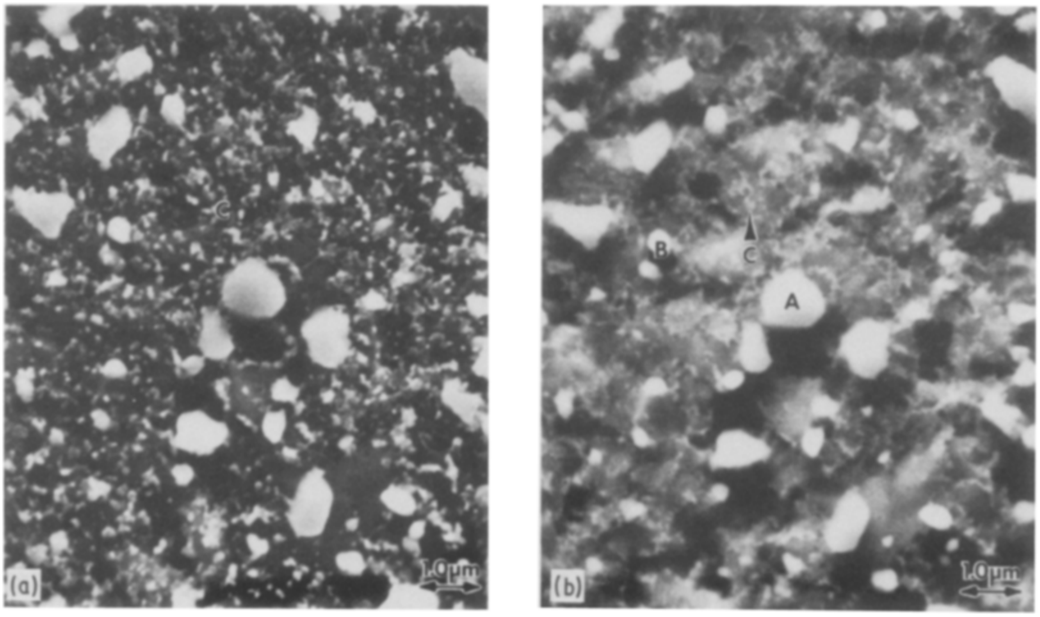


Figure 11 (a) SEI and (B) BEI scanning electron photomicrographs of Markomet 1483 aged at 773 K. (A) Chromium-rich; (B) (titanium, chromium, molybdenum)-rich; (C) titanium-rich borides.

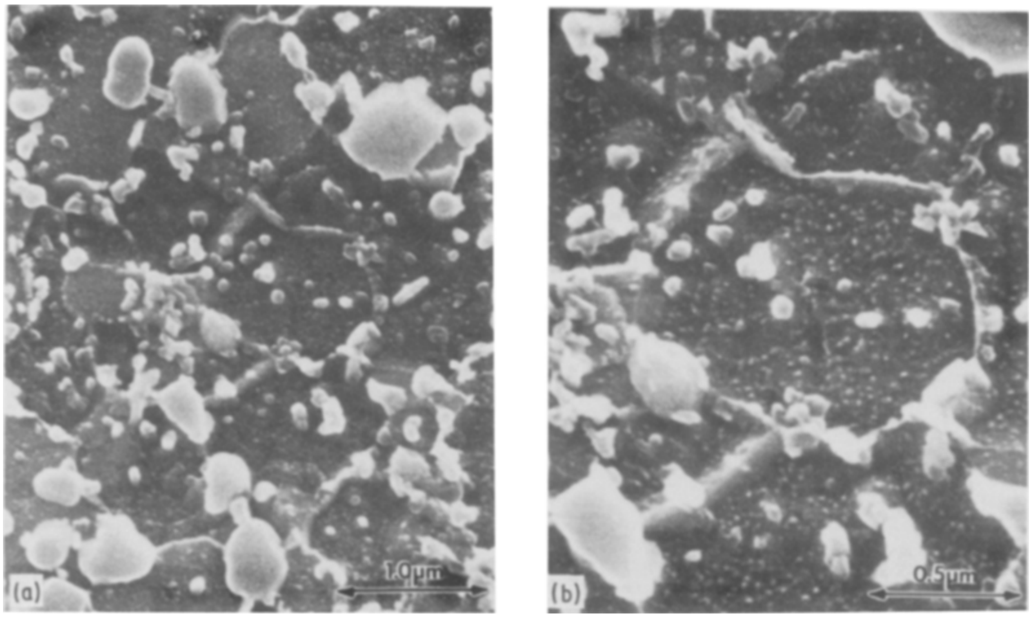


Figure 12 (a), (b) High-magnification scanning electron (SEI) photomicrographs of Markomet 1483 aged at 773 K.

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