ANALYSIS OF FRACTURE SURFACES OF Mo-ALLOYS WITH CARBIDE DISPERSIONS

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Mo-alloys with various contents of Ti, Zr, Hf and C were tested. Since the type of binding in carbides and oxides has an influence on forming procedures and mechanical properties, the fracture surfaces were investigated for such inclusions by means of scanning electron microscopy and Auger electron spectroscopy.

INTRODUCTION

Among powder-metallurgy Mo-alloys, the carbide-dispersion hardened alloy TZM (for composition see Table 1) is the most important (1,2). Its advantage, compared to Mo and other high-temperature materials, is its high strength in relation to its low density. The strength component which comes from cold working is kept up to 1200 $^\circ$C even in long-time applications. These properties have so far not been obtained by other metallic materials. One application of TZM, where no other material performs better, is in tools for the deformation at 900 to 1100 $^\circ$C of superplastic superalloys and Ti-alloys. As the requirements for tool materials grow, a development program for even more creep-resistant Mo-alloys has been initiated. A series of new alloys (see Table 1) with additions of Ti and Zr, Zr and Hf, Hf only, and with various carbon contents were produced using powder metallurgy methods. Sintered rods of the three alloy groups were reduced by 60% in area by rotary swaging. Fig. 1 shows the tensile data at room temperature and at 1100 $^\circ$C. Table 1 includes also the time leading to creep rupture. The results show the superiority of the alloys TZC and ZHM.

It would be interesting to classify the reactions of Ti, Zr and Hf, or of their combinations with C, with Mo as the matrix material, and with O or possibly N as ever present reactants.

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TABLE 1 - Composition of Alloys and Time to Fracture in Creep

Alloy	wt.% Ti	wt.% Zr	wt.% Hf	wt.% C	Time to fracture (min) at 450 N/mm^2
TZM	0.5	0.07	–	0.05	~1
TZC	1.0	0.14	–	0.10	2094
ZHM	–	0.72	0.14	0.05-0.10	2100-2800
MHC	–	–	0.2-3.0	0.05-0.40	150-460

As a first attempt to understand the behaviour of the alloys we looked at microstructures and fracture surfaces by means of various methods: we used light microscopy, the microprobe analyzer, the scanning electron microscope (SEM), and Auger electron spectroscopy (AES).

THE ANALYSIS

In order to obtain fracture surfaces, we broke the specimens perpendicular to the working direction in liquid nitrogen. The fracture mode is almost entirely transcrystalline. While this is of course common in as-worked structures (3), we were surprised to find it even in the recrystallized state.

Although the maximum temperature in the mechanical tests was 1100 °C, we investigated in addition to the as-worked condition also materials which were annealed at 1500 °C and 2200 °C. The latter annealing temperature is known to embrittle Mo-alloys considerably.

Light Microscopy

In Fig. 2a, for the as-worked state, a few particles of white colour can be resolved along grain boundaries, along with occasional grayish inclusions. An annealing treatment at 1500 °C for one hour (Fig. 2b) leads in general to a more or less polygonized grain structure, and to the beginning of recrystallization. After annealing at 2200 °C the grain is fully recrystallized (Fig. 3). The main feature of the high-temperature annealing is the appearance of grain-boundary precipitates. White particles and platelets are abundant, and fill the grain-boundary areas almost entirely. These general features are common for all the three alloy groups. TZM and TZC exhibit a more pronounced grain growth than the other alloys.

In MHC-alloys with high Hf-contents, which are recrystallized at 2200 °C, there are small, elongated precipitations visible, oriented in two main directions within each grain (Fig. 4). They indicate that some submicroscopic precipitation occurs at the early stages of annealing, and that precipitation hardening has to be considered as one hardening mechanism.

Microprobe Analysis and Scanning-Electron Microscopy

The next step was to identify the particles and grain-boundary precipitates in the various alloys. First we concentrated on the larger greyish inclusions which appear randomly distributed within the grains and also in grain boundaries. According to the microprobe analysis of microsections they are oxides; no carbon could be found. In TZM and TZC they contain mainly Zr. Only small peaks of Ti were seen in the energy-dispersive X-ray analyzer of the SEM. While these oxidic praticles are rounded in TZM and TZC (Fig. 5), they have sharp corners and edges in MHC (Fig. 6). In MHC we identified them as containing Hf by means of the microprobe analyzer on microsections, as well as in the SEM on fracture surfaces. Hf is oxidized during the sinter process, and the oxides have a high melting point of 2800°C. They are fractioned during the working process into smaller pieces (see Fig. 6) and are never remelted and rounded again, not even at the high recrystallisation temperature. In ZHM-alloys, both types of oxidic particles (round and sharp-cornered) are present, and each type contains Zr as well as Hf. We measured consistently that the impuls rates of Hf exceed those of Zr in the rounded particles. Since no Hf-standard was available, it is impossible to judge whether the Zr/Hf-ratio of the impulse rates is directly proportional to the ratio of the actual concentrations. It seems more likely that the ratios are inversely proportional if we remember that in ZHM the Zr-content exceeds the Hf-content, and that in MHC the broken particles (those which never melt) are those which contain Hf.

As mentioned before, white grain-boundary inclusions can preferably be found after the 2200°C-anneal. From the microprobe analyzer we obtained indications that the carbon (but not the oxygen) concentration is raised in the grain boundaries. At higher magnification in the SEM, it is not possible to confirm the carbidic nature of the grain-boundary particles, since the SEM is not able to detect light elements. But we proved in the SEM that in TZM and TZC the white particles consist of Ti and apparently also of Mo. In ZHM, Hf is the main element; only sometimes we find Zr. In MHC, we could distinguish between white individual particles containing Hf, and others (e.g. plate-like) showing only Mo-signals.

The small precipitations in MHC-alloys of high Hf-content, shown in Fig. 4, were identified from microsections in the SEM as Hf-containing. They are perhaps the particles we see regularly on transcrystalline fracture surfaces as in Fig. 7, where we found most of them as containing Hf, some as containing Mo. The foto is in fact remarkable since it pictures three possibilities. The X-ray spectrum from the SEM in Fig. 8 proves that the particle A consists of Hf, particle C of Mo. The particle B must be a conglomerate of the two types: we see a reasonably strong Mo $L\alpha$ - line, the typical Hf $L\beta_1$ - and Hf $L\beta_2$ - lines, while the low-energy Hf $M\alpha$ - line is very little pronounced. We take this as an indication that a Hf-containing particle is covered by a Mo - containing particle which strongly attenuates the Hf M -radiation. We have now partly correlated the over-aged precipitates in the grains of Fig.4 with the Hf-content and thus with the alloy's capability of precipitation hardening. According to Fig.1 it is, however, the alloy ZHM which is best. Apparently Zr/Hf - inclusions are important for optimum precipitation hardening.

Auger Electron Spectroscopy

AES-spectra of large inclusions usually show peaks of Hf together with those of Mo (probably from the matrix), and pronounced peaks of carbide, oxide and even nitrogen (Fig.9a). The surrounding matrix as well as some (grain-boundary?) inclusions display only Mo, carbide, oxide and sometime nitrogen, but no Hf (Fig.9b). Since the diameter of the primary electron beam of the equipment is about 5 μm, this can be explained by the presence of small inclusions of (preferably) Mo-carbide and/or oxide. Within the matrix of TZM, TZC and ZHM, Ti respectively Zr could not be found because of their low bulk concentration, partly because their spectra tend to overlap with strong peaks of the matrix Mo.

In recrystallized specimens, large areas could be found consisting presumably of free carbon (Fig.10) with almost no traces of Mo or even oxygen. Their presence can not be explained at the moment, but is confirmed by preliminary X-ray diffraction studies.

Thermodynamical Considerations

In agreement with the previous results, thermodynamic calculations seem to confirm that both TZM and TZC should contain preferably Zr-oxides and less Ti-oxides (the free enthalpy of formation ΔG at 2000 K is -714 kJ/mol for ZrO_2, and -334 kJ/mol for TiO_2). We also calculated the free enthalpies of mixing of the systems Mo-Hf, Mo-Zr and Mo-Ti. Their ΔG - values, which all are about -50 kJ/mol, were compared with those from Mo-, Ti-, Zr- and Hf-oxides and carbides, all ranging from -100 kJ/mol down to -750 kJ/mol. The solid solution is much less stable than the oxides and carbides, and this shows that most of the alloying elements should be found in oxides and carbides, and not so much in the matrix. Which one of Zr or Hf (when they are both present in one alloy) forms oxides or carbides is app arently not so much determined by thermodynamics, but by the distribution and availability of the element.

CONCLUSION

The high-temperature properties of the conventional Mo-alloy TZM can be improved by additions of Ti and Zr, or by Zr and Hf. Light and scanning electron microscopy, a microprobe analyzer and Auger electron spectroscopy were used as tools to shed light on the complex reactions of the alloying metals with the Mo-matrix, and with oxygen and carbon. Oxides and carbides are favoured over the formation of solid solutions. However, it is not always true that those metals combine exclusively with oxygen and carbon which are thermodynamically best suited to do so. Oxi-carbides have not been found. Segregation within the bulk of grains indicates that precipitation-hardening affects the strength. The presence of free carbon has to be considered as a possiblity, and should be taken into account in heat-treating procedures.

REFERENCES

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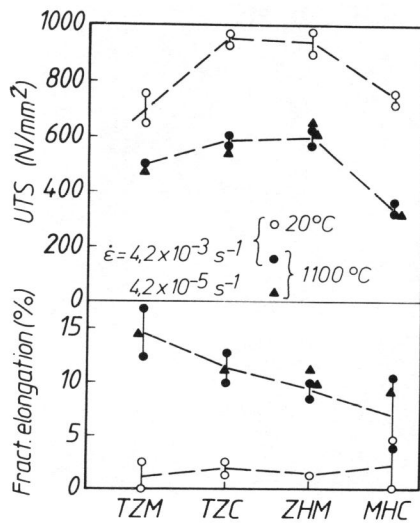3. Pink E. and Sedlatschek K., 1969, Metall 23, 1249
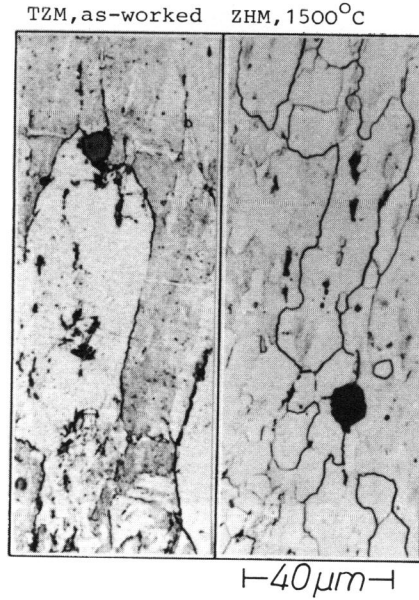
Fig. 1. Results from tensile tests with Mo-alloys.

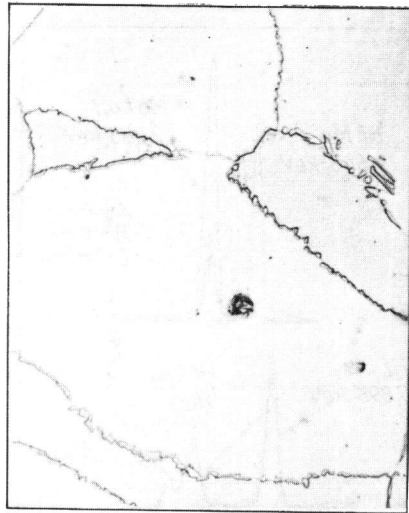Fig. 2. Deformation structure and partly recrystallized structure.
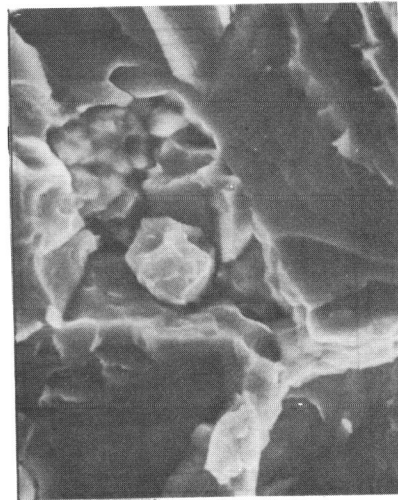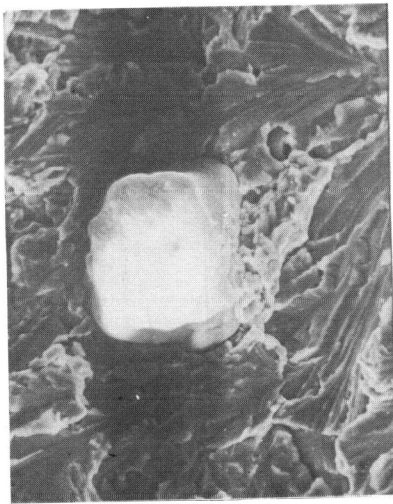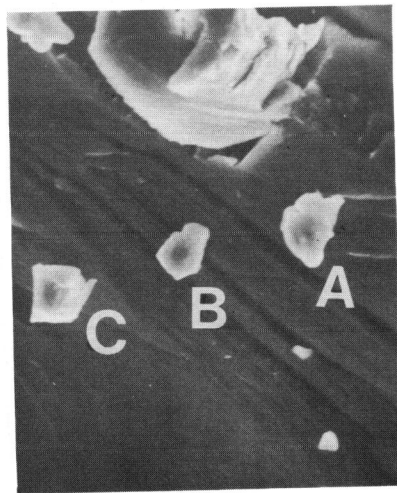

Fig. 3. TZC, recrystallized at 2200 °C.

Fig. 4. MHC with 3% Hf, recrystallized at 2200°C.

347

├─ 10 μm ─┤

Fig. 5. ZHM, Zr(Hf)-oxide.   Fig. 6. ZHM, Hf(Zr)-oxide.
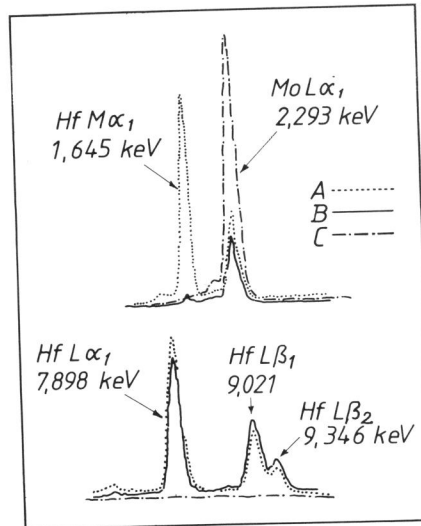

├─ 10 μm ─┤

Fig. 7. MHC, small carbide par-   Fig. 8. SEM-spectra of particles
ticles.   A, B and C of Fig. 7.

348

271 382 511 1624 1678 2044 eV

carbide N oxide Hf Mo

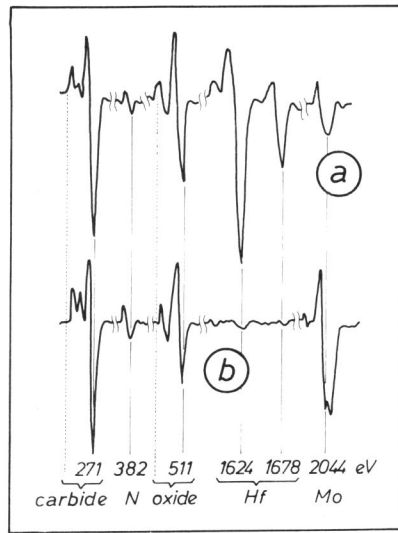186 221 382 511 eV
Mo Mo N O
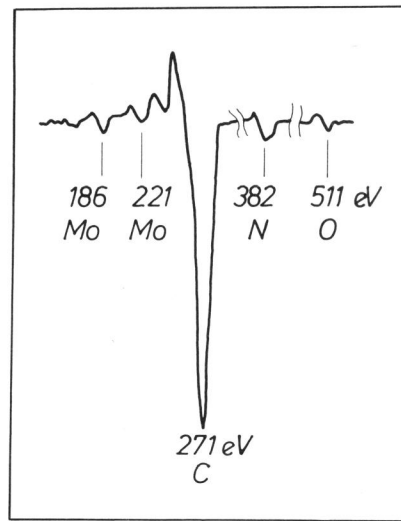
271 eV
C

Fig. 9. AES; spectra of an in-
clusion (a) and the Matrix (b).

Fig. 10. AES; spectrum of free
carbon.