Effect of Molybdenum Content on Mechanical Properties
of Sintered PM Steels

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Abstract: A large number of PM applications require sintered components capable of withstanding high operational static and dynamic stresses. High sintered density is one of the key parameters to enhance dynamic properties together with appropriate microstructure. Low alloy Mo-steel powders present interesting attributes since this alloying element only slightly affects powder compressibility and is very efficient to increase hardenability and hence mechanical properties. Furthermore, key elements such as Ni and Cu admixed to the base steel powder or diffusion bonded to the steel particles during the annealing treatment also improves the mechanical properties through modification of the microstructure. This paper illustrates the tensile and dynamic properties of low alloy steel powders containing various levels of pre-alloyed molybdenum. The effect of either admixing or diffusion bounding Ni and Cu to these Mo-steels is also discussed particularly with respect to axial fatigue properties and strength. Comparison with results obtained with other types of fatigue specimens and/or testing methods is also presented.

Introduction

The object of this study was to evaluate the influence of the level of Mo in steel powders from 0.5 to 1.5% on the tensile and dynamic properties of mixes containing 4% Ni, 1.5% Cu and 0.6% graphite at 7.0 g/cm. Particular attention was paid to the axial fatigue properties. In particular, the S-N curves and the fatigue limit at 10^7 cycles were determined for five different mixes. A second objective of this study was to verify if the particle size of the admixed copper has an effect on the tensile and fatigue properties of such mixes. Indeed, it is known that the copper affects the size of porosity, which in turn affects the fatigue performance of sintered components [1]. Smaller pore size in association with rounded pores improves the fatigue performance at a given density. Both regular and binder-treated mixes were prepared with a pre-alloyed 0.5% Mo steel powder and containing respectively a regular and a finer copper powder. They were evaluated and compared to a diffusion-bonded powder based on 0.5% pre-alloyed Mo and with 4%Ni and 1.5% Cu partially diffused with steel particles.

Experimental Procedure

Water atomized pre-alloyed Mo steel powders containing either 0.5% Mo (ATOMET 4001), 0.85% Mo (ATOMET 4401) or 1.5% Mo (ATOMET 4901) were selected for this study together with a diffusion-bonded powder, ATOMET DB48 containing 0.5% Mo, 4%Ni and 1.5%Cu. The three pre-alloyed Mo steel powders were admixed with 4% nickel, 1.5% copper, 0.60% natural graphite and 0.75% wax, while the diffusion-bonded powder was admixed with 0.60% natural graphite and 0.75% wax. A commercial grade of Cu having an average diameter D_{50} of about 40μm was used in all of these powder mixes. In

addition to these standard mixes, a binder-treated mix made with the 0.5% Mo steel powder was prepared by using the QMP patented binder technology [2]. A fine commercial Cu grade having a D_{50} of ~15 to 20 μm was used in this mix. The chemical composition and characteristics of the pre-alloyed and diffusion-bonded powders evaluated in this study as well as the mixing technique are given in Table 1.

Table 1. Characteristics of the steel powders and pre-mixes evaluated in this study.

Mix name/ Steel powder	Type of mix	Pre-alloyed elements, wt%		Diffusion elements, wt%		Admixed elements, wt%			Flow, s/50g	A.D., g/cm³
		Mo	*Mn*	*Ni*	*Cu*	*Ni*	*Cu*	*Graphite*		
R-0.5Mo (ATOMET 4001)	Regular	0.5	0.15	-	-	4.0	1.5 (reg)	0.6	37.0	3.02
BT-0.5Mo (ATOMET 4001)	Binder-treated	0.5	0.15	-	-	4.0	1.5 (fine)	0.6	31.6	3.09
DB-0.5Mo (ATOMET DB48)	DB/ Regular	0.5	0.15	3.9	1.5	-	-	0.6	35.0	3.05
R-0.85Mo (ATOMET 4401)	Regular	0.85	0.15	-	-	4.0	1.5 (reg)	0.6	36.3	3.00
R-1.5Mo (ATOMET 4901)	Regular	1.5	0.15	-	-	4.0	1.5 (reg)	0.6	35.1	3.08

The mechanical tests were carried out at a density of 7.0 g/cm³. Standard ISO flat axial fatigue specimens were used to evaluate the fatigue properties for all materials. The fatigue specimens were pressed to 7.0 g/cm³, sintered 25 min. at 1120°C in a nitrogen based atmosphere and tempered 60 min. at 205°C in air, under the same conditions as the other specimens. Specimens were polished to a smooth finish. Axial fatigue was tested in a fully reversed tension-compression loading mode (R= -1) with a sine waveform. A sample that survived more than 10^7 cycles was considered a run-out. The staircase method was used to determine the mean fatigue limit where 50% of the specimens are expected to survive.

Sintered and tensile properties

Results of the transverse rupture and tensile tests on tempered specimens are summarized in Table 2. After sintering and tempering, the rupture strength and the apparent hardness initially increased between 0.5 and 0.85% Mo and then leveled off above 0.85% Mo. As expected, the tempering treatment reduced apparent hardness and increased TRS for all the materials.

An identical trend was also observed with the UTS and YS, which first increased from 0.5 to 0.85% Mo and then leveled off above 0.85%. The elongation followed the opposite trend, decreasing from 1.7 to 1.0%, when increasing the Mo content from 0.5% to 1.5%. The reduction in elongation was more pronounced between 0.5 and 0.85%.

The sintered and tensile properties of the regular and binder-treated materials made with a 0.5% Mo steel powder and a diffusion-bonded material were quite similar. Slightly higher transverse rupture strength was obtained with the diffusion-bonded material. However, there was no significant difference in tensile and yield strength between these materials. The elongation of the diffusion-bonded powder mixes was also slightly lower.

Table 2. Transverse rupture and tensile properties of pre-alloyed Mo steel powders containing 4% Ni, 1.5% Cu and 0.6% graphite at 7.0 g/cm³.

Mix ID	TRS, MPa	App. Hard, HRC	DC vs die size, %	DC vs green size, %	UTS, MPa	YS, MPa	Elongation, %
R-0.5Mo	1644	20	0.02	-0.14	854	545	1.7
R-0.85Mo	1762	26	0.01	-0.15	924	580	1.2
R-1.5Mo	1791	27	-0.07	-0.23	937	587	1.0
R-0.5Mo	1644	20	0.02	-0.14	854	545	1.7
BT-0.5Mo	1688	21	-0.06	-0.22	845	569	1.6
DB-0.5Mo	1781	22	0.01	-0.17	848	544	1.2

Microstructure and Porosity

Fig. 1 shows the typical microstructure for the 0.5, 0.85 and 1.5% Mo materials admixed with 4%Ni, 1.5%Cu and 0.6% graphite. The microstructure is typical for this type of formulation, specifically a heterogeneous microstructure constituted of areas with divorced pearlite, fine pearlite/bainite, martensite and Ni-rich retained austenite. The microstructure within the steel
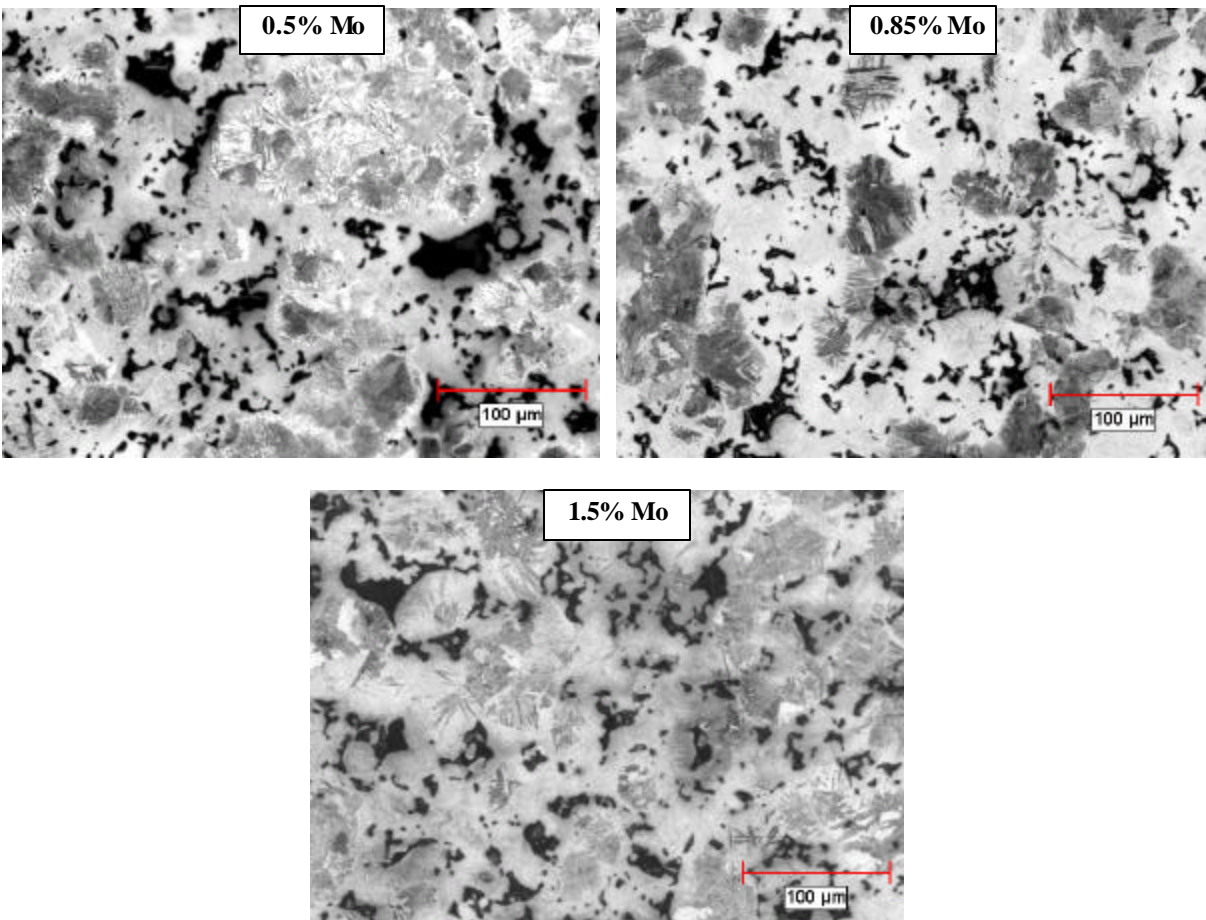

Fig. 1 Typical microstructure of regular mixes made with 0.5, 0.85 and 1.5% Mo steel powders admixed with 4%Ni, 1.5%Cu and 0.6% graphite. (Specimens pressed to 7.0 g/cm³).

particles, where nickel did not diffuse, changed gradually from divorced pearlite/pearlite/bainite to bainite/martensite as the amount of Mo increased.

It is well known that the admixed copper particles melt during sintering at about 1080°C and penetrate into the steel particles. This diffusion leaves pores behind. The particle size of the copper should therefore affect the size of the residual pores. Fig. 2 shows the cumulative pore count frequency as a function of the pore length (determined by the maximum size of pores) in sintered specimens along with micrographs showing the porosity distribution. Specimens made with materials that were admixed with a regular grade of copper show a similar pore frequency distribution. The longest pores analyzed in these specimens were in the range of 190 to 200 µm. However, in the binder-treated and diffusion-bonded materials, the number of pores per unit area above 50 µm was significantly lower. In fact, the slope of the frequency distribution shown in Fig. 2 was significantly steeper for these materials than for the regular mix. As a result, the longest pores observed in sintered specimens were respectively about 140 and 155 µm for the binder-treated and the diffusion-bonded materials. These analyses clearly show that the grade of copper used has a strong influence on the pore size distribution.
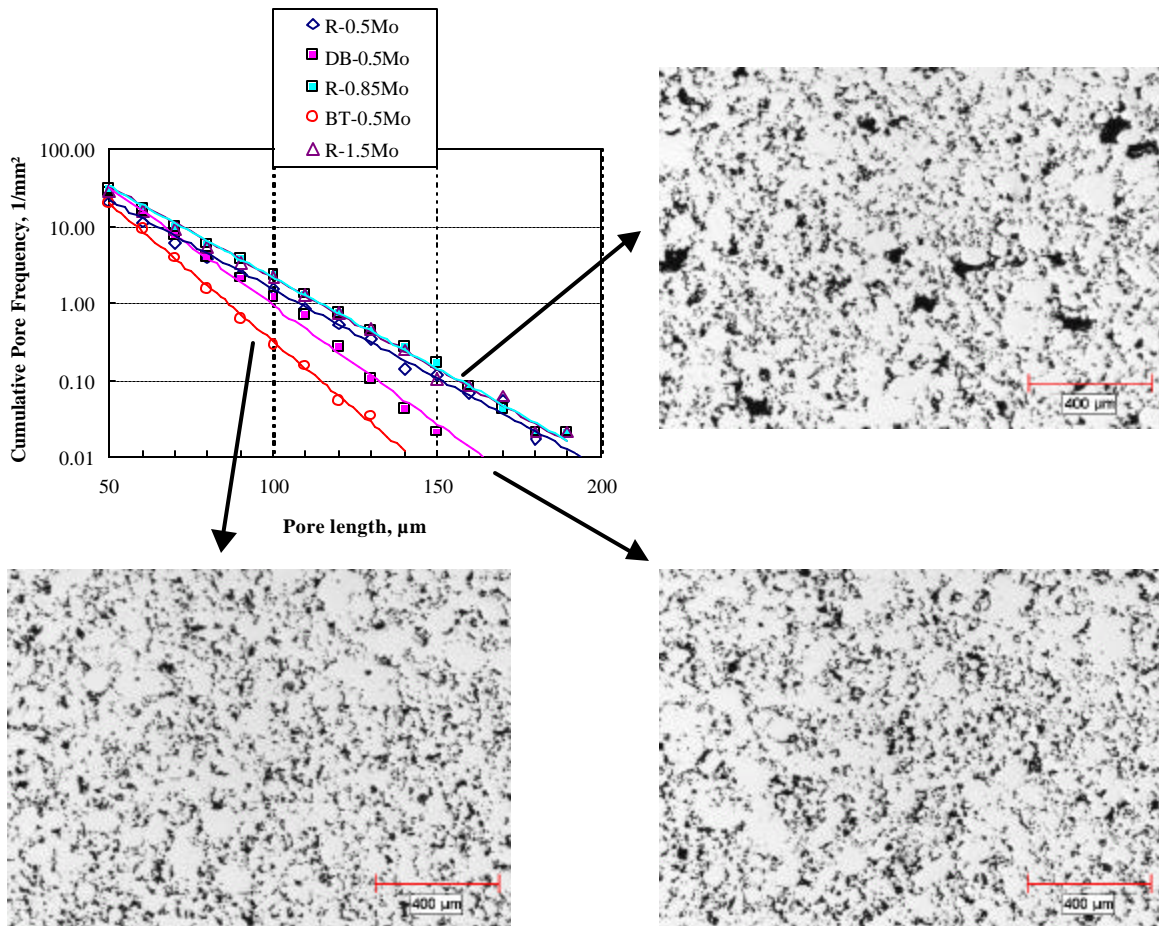

Fig. 2 *Variation of the cumulative pore frequency (number of pores per unit area) for the regular, binder-treated and diffusion-bonded powders along with micrographs showing the porosity.*

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Fatigue properties

S-N curves (influence of Mo content and type of mix)

Fig. 3a shows the S-N curves obtained for the regular mixes containing various levels of pre-alloyed Mo while Fig. 3b shows the S-N curves for the regular, binder-treated and diffusion-bonded mixes containing about 0.5% pre-alloyed Mo. Equations of the type log (S) = A + B*log (N) where S is the stress amplitude, N the number of cycles to reach failure and A and B coefficients was used in this work to characterize the S-N curves. It can be seen in Fig. 3a that increasing the Mo content from 0.55 to 0.85% is clearly beneficial to the fatigue properties by shifting the S-N curves upward or to the right. However, no significant difference in the response to the cyclic loading was found between 0.85 and 1.5% Mo, both steel powders giving almost identical S-N curves.

No essential difference in the S-N curves was seen for the 0.5% Mo series, Fig. 3b. Both the regular and binder-treated mixes gave almost identical S-N curves while the S-N curve for the DB-0.5 Mo material was shifted slightly upward or to the right. The average number of cycles to failure for a given stress amplitude was lower for all of the 0.5% Mo series materials compared to the 0.85 and 1.5% Mo series. It is clear based on these results that the use of a finer copper, which resulted in a significantly lower quantity of pores larger than 50 μm, has no significant effect on the S-N curve obtained on specimens pressed to 7.0 g/cm³. However, the use of fine copper could be beneficial at higher densities.

The variability of the fatigue-life can be expressed by the standard deviation or the standard error of the S-N curve equations [3]. These values were computed for each material and are given in Table 3 along with the parameters of the equations. The regular mix made with a 0.5%Mo steel powder (R-0.5Mo) showed the largest standard deviation amongst all the materials tested while the binder-treated material (BT-0.5Mo) showed the lowest standard deviation. An F-test showed that the difference in standard deviation between both materials was statistically significant at a confidence limit of 95%. Hence it appears that the use of a finer copper, which significantly reduces the number of large pores, combined with binder-treatment decreases the variability in fatigue-life. The differences in variability between the binder-treated mix and the other materials were not large enough to be statistically significant at a 95% confidence level. Nonetheless, the F-tests indicated that the probability that there exists a difference between the binder-treated material with fine copper and the other materials is 75% or higher. More tests would be needed to clearly confirm if the difference in variability is significant. In the same manner, the differences in standard deviation between the regular 0.5% Mo mix showing the largest variability and the other regular mixes with 0.85 and 1.5% Mo were not large enough to conclude with a level of confidence of 95% that these differences were significant. Nevertheless the probability that such differences are significant still remains high (between 77 and 83%).
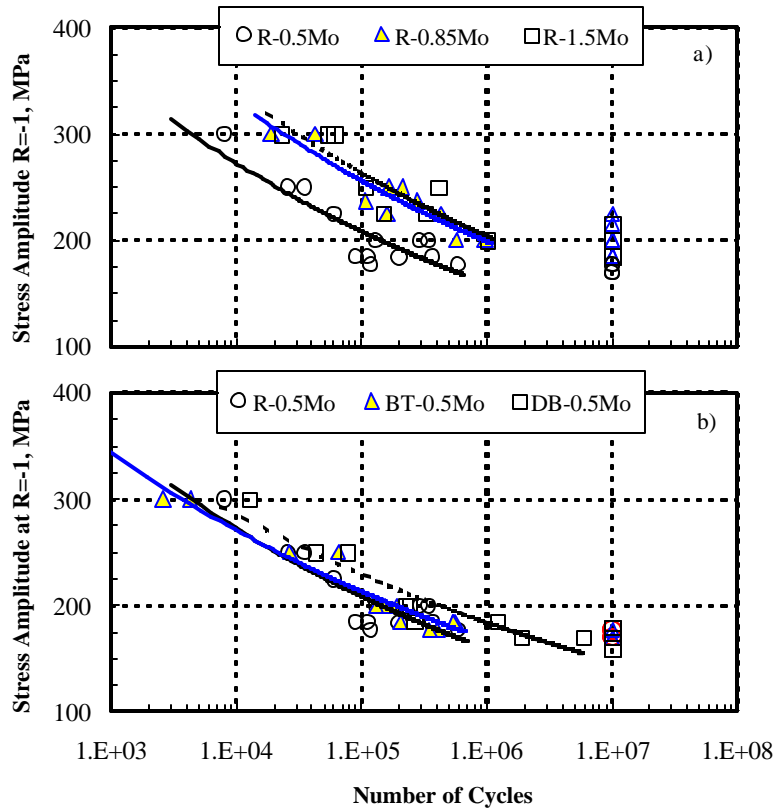
Fig. 3 *S-N curves obtained at 7.0 g/cm³ for Mo steel powder admixed with 4%Ni, 1.5% Cu and 0.6% graphite. a) Effect of molybdenum content. b) Effect of powder manufacturing.*

Table 3. Parameters for the S-N curve equations.

Mix	Log (S) = A + B*log (N)				
	A	*B*	*Std dev.*	*R value*	*R² value*
R-0.5Mo	2.902	-0.1167	0.0372	0.8648	0.7479
R-0.85Mo	2.959	-0.1101	0.0290	0.9263	0.8581
R-1.5Mo	2.976	-0.1111	0.0297	0.8829	0.7795
R-0.5Mo	2.902	-0.1167	0.0372	0.8648	0.7479
BT-0.5Mo	2.847	-0.1037	0.0227	0.9657	0.9326
DB-0.5Mo	2.839	-0.0958	0.0325	0.9355	0.8752

Fatigue limit

The axial fatigue limits at 50% and 90% survival as well as the tensile properties are reported in Table 4. Fatigue limits at 50 and 90% survival are also shown in Fig. 4. The fatigue limit at 50% survival ranged from 170 to 210 MPa, resulting in a fatigue limit to tensile strength ratio of 0.20 to 0.23. Raising the Mo content from 0.5 to 0.85% was beneficial for the fatigue limit, which increased from about 175 MPa to 210 MPa. However a further increase to 1.5% Mo did not raise the fatigue endurance, which remained unchanged at 210 MPa. The higher performance of the 0.85 and 1.5% Mo steel powder is likely due to the change in microstructure from primarily pearlite (fine and divorced) to predominantly bainite/martensite [4].

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Table 4. Tensile and axial fatigue limits of regular and diffusion-bonded Mo steel powders containing 4% Ni, 1.5% Cu and 0.6% graphite at 7.0 g/cm³.

Mix	UTS, MPa	YS, MPa	App. Hard. (test bars), HRC	Fatigue limit 50% survivals, MPa	Fatigue Limit 90% survivals, MPa	Endurance ratio FL$_{50\%}$ /UTS
R-0.5Mo	854.0	544.7	19.0	177	162	0.21
BT- 0.5Mo	834.4	566.5	19.7	176	161	0.21
DB- 0.5Mo	847.7	543.6	22.3	168	160	0.20
R- 0.85Mo	924.2	579.8	26.0	208	187	0.22
R- 1.5Mo	936.8	587.2	26.0	211	183	0.23

No significant difference in the fatigue limit was obtained among specimens made with powder mixes containing 0.5% Mo. In all cases, the fatigue limit ranged from 170 to 180 MPa. This indicates that the use of fine copper in the binder treated mix did not have the anticipated beneficial effect on the fatigue limit for specimens pressed to 7.0 g/cm³. Previous studies have shown that porosity plays a key role in fatigue crack initiation. Specifically, large pores are mainly responsible for fatigue crack initiation and propagation. These studies also demonstrated that the use of finer copper powder significantly reduced the size and number of pores larger than 50 μm. However, this had no significant effect on fatigue properties. A possible explanation is, that at 7.0 g/cm³, the volume fraction and thus, the quantity of large pores, which could play a role in fatigue crack initiation, remains sufficiently high to affect fatigue. Moreover the microstructure is another factor that strongly affects the fatigue properties. Indeed, at relatively low density, 7.0 g/cm³ or less, the strength of the sintering necks are believed to control fatigue [5]. However, it is clear from this study that modifying the microstructure by increasing the Mo content was the major factor influencing the fatigue endurance limit.

Values reported in Table 4 and Fig. 4 are lower than the fatigue limits obtained with the RBF test method and published in previous studies [6,7].
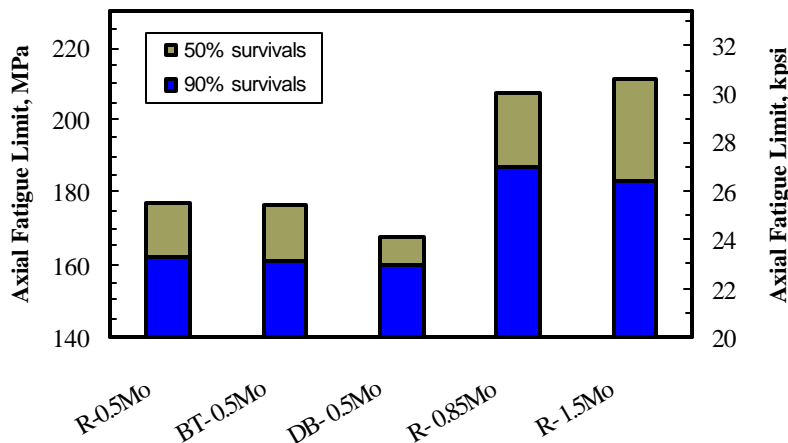

Fig. 4 Fatigue limit at 50 and 90% survival measured by the staircase method for various pre-alloyed Mo steel powder mixes at 7.0 g/cm³.

It is known that the test method selected to measure the response of a material to cyclic loading has a strong influence on the results. Lin et al showed that the axial fatigue limit corresponded to about 78 to 92% of the RBF limit for various as-sintered and heat-treated materials [8]. The major reason for such a difference is that during RBF tests, the stress is maximized only at the circumference of the specimens.

However in the axial fatigue test, the stress is similar throughout the tested surface area. In axial fatigue testing, cracks can initiate far below the surface if significantly large defects are present, even though fatigue cracks usually initiate at the surface or close to the surface for these types of specimens [9].

The test specimen also has a significant effect on the result. Indeed, in axial fatigue testing, round specimens such as those used in RBF tests can be used. This type is usually machined from sintered blanks. The specimen surface consists of a thin layer of smeared material free of porosity [9]. In addition, there are no stress raisers along the circumference. In contrast, the surface of a flat bar specimen, used in this study, is in the as-sintered condition, which contains open porosity. Moreover, flat rectangular bars have corners that act as stress raisers. Fracture analyses clearly showed that most of the fatigue cracks initiated from a corner and propagated to the opposite corner. Fig. 5 shows several SEM micrographs of the fracture surface of a fatigue specimen made from mix R-0.5Mo. Fig. 5a shows a general overview of the fracture surface. The fatigue crack likely initiated from a large pore at the corner in region C, Fig. 5b. Fig. 5c shows region A close to the initiation site. The fracture surface is typical of a fatigue crack-propagating mode with evidence of striations. Finally, region B shown in Fig 5d was a typical overload failure with evidence of ductile fracture. Therefore, the presence of corners in flat specimens likely contributed to reduce the fatigue limit compared to that of machined round specimens.
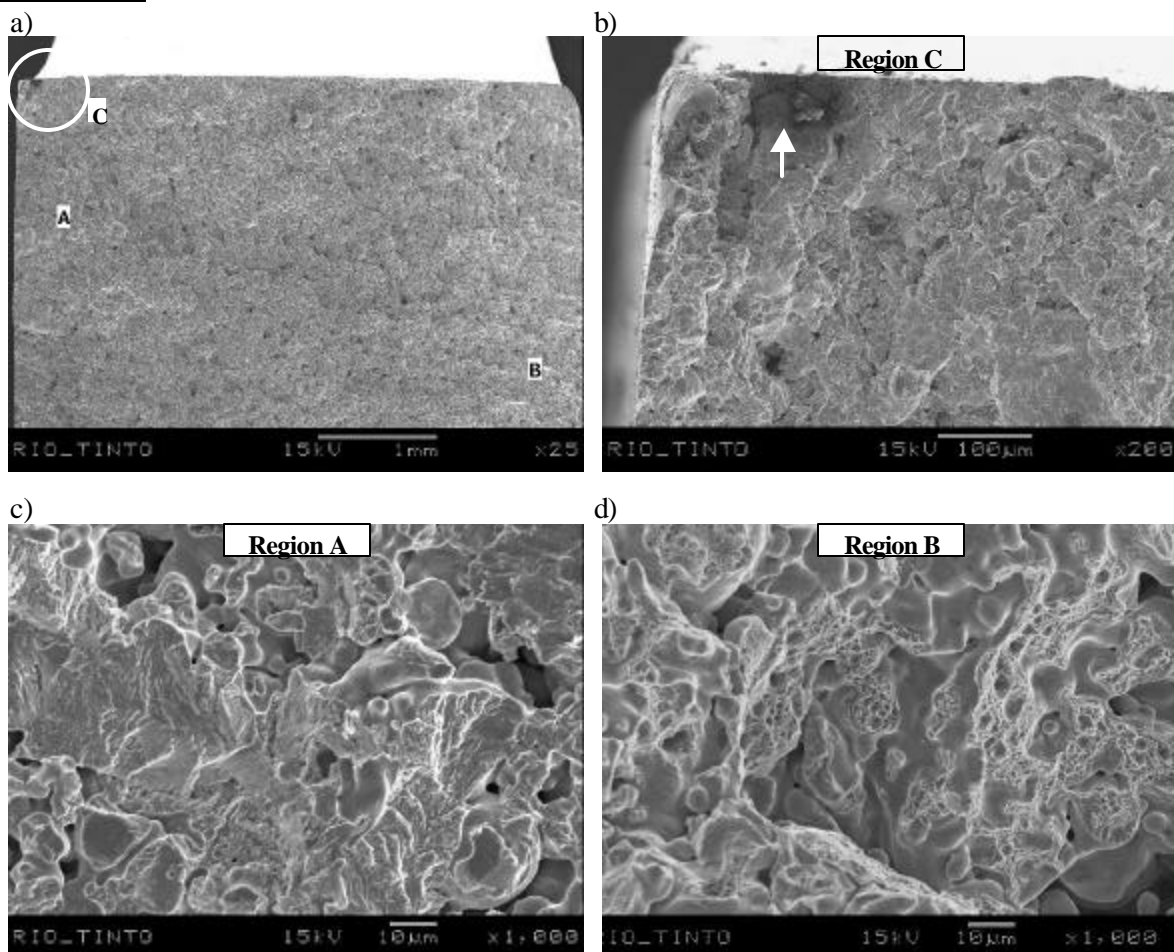
Conclusions

Fig. 5 *SEM Micrographs showing the fracture surface of a fatigue test sample (Mix R -0.5Mo).*
a) Fracture surface at low magnification. b) Zone C: Fatigue crack likely initiated from a pore at the corner. c) Zone A: typical fatigue-propagating fracture mode. d) Zone B: Final ductile overload.

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The following conclusions can be drawn from this study:

- Increasing the Mo content from 0.5 to 0.85% is beneficial for the transverse rupture, tensile and fatigue properties but slightly decreases the ductility.
- A further increase of the Mo content from 0.85 to 1.5% has no significant effect on the static and dynamic properties.
- The beneficial effect of increasing the Mo content from 0.5 to 0.85% on fatigue properties is due to the transformation of the microstructure from divorced pearlite/pearlite to bainite/martensite.
- Using a fine copper addition decreases the number of pores larger than 50 µm. However at a density of 7.0 g/cm³ this does not affect the static properties except for the dimensional change, which was more negative by about 0.08%.
- The pore size reduction caused by the use of finer copper results in less variation during cyclical loading. However at 7.0 g/cm³ this has no influence on the S-N curve or fatigue limit. It is believed that use of finer copper will be beneficial at higher densities.
- No significant difference in the fatigue properties was seen between a low-alloyed Mo steel powder admixed with Ni and Cu and a diffusion-bonded powder of the same composition.
- The axial fatigue limits obtained with flat specimens are about 25% lower than those measured by the RBF method.

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