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IMPROVEMENT OF MECHANICAL PROPERTIES BY OPTIMIZATION OF Cr AND Mo CONTENTS IN xCr-yMo-9Ni-2Cu-1Ti-1V STEEL

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ABSTRACT

The effects of Chromium and Molybdenum quantities in the range of 9-13 and 3-6 wt% respectively on the microstructural characteristics and mechanical properties of xCr-yMo-9Ni-2Cu-1Ti-1V steel was investigated in this research. According to the results obtained in this work, solution treated specimens with lower contents of Cr and Mo had austenitic-martensitic structure. But when increasing these elements, some amount of ferrite was formed. Applying plastic deformation leads to the transformation of austenite to martensite. Increasing Cr content up to 10 wt%, resulted in the improvement of mechanical properties without any substantial change in the microstructure. On the other hand, an increasing Cr content in the range of 11-13 wt% caused a decrease in strength and ductility due to the formation of ferrite in the structure. Besides, Mo showed the same behavior as Cr and when Mo content was 5 wt%, the optimum mechanical properties obtained.

Key words: Stainless Steel, Chromium, Molybdenum, Mechanical Properties

1. INTRODUCTION

The precipitation hardened stainless steels containing substantial amounts of Cr, Ni, Mo, Cu and Ti, have been developed for about 60 years. The high strength combined with good fracture toughness observed in these steels, is said to be [1-3] due to the precipitation of fine intermetallic phases containing Ni, Mo, Cu, Ti, Al, W, V and Nb in the low carbon martensitic matrix during aging. Most applications of these alloys have been reported in the petrochemical industry, aerospace industry, and medical tools.

In these types of steels the basic elements such as Cr, Ni and Mo play the major role to identify the microstructure, mechanical properties and corrosion resistance. According to the chemical composition, after hot deformation their structure can be martensite, unstable austenite or the mixture of the two. In some conditions it may also contain some ferrite. By applying stress or strain, the unstable austenite under the M_D temperature ($M_{D30/50}$, the temperature at which 50 vol% of martensite is formed by deformation after true strain of 30%) and above the M_s temperature (the start temperature of martensite formation) transforms to martensite. This type of martensite is called Deformation

Induced Martensite, DIM [4]. The formability and work hardening coefficient of these steels are greatly influenced by martensitic transformation during straining [5-8].

Some researches [9-11] showed that changing the amount of alloying elements in stainless steels may cause a large variation in the microstructure, due to the different stabilizing character of each element. Different kinds of models were suggested to predict the microstructure of stainless steels. A number of mathematical models have been developed [4, 9-13] by means of which ferrite stabilizing elements could be expressed as an equivalent Chromium content (Cr_{eq}), and the austenite stabilizing elements as an equivalent Nickel content (Ni_{eq}). The following relationships are proposed for Cr_{eq}:

$$Cr_{eq} = Cr + Mo + 0.5Nb + 2Ti \qquad (1\text{-}a)\ [10]$$

$$Cr_{eq} = Cr + 1.5Mo + 1.75Nb + 1.5Ti + 5V + 0.75W + 2Si + 5.5Al \qquad (1\text{-}b)\ [11]$$

$$Cr_{eq} = Cr + 1.2Mo + 0.14Nb + 2.2Ti + 2.27V + 0.72W + 0.48Si + 2.48Al \qquad (1\text{-}c)\ [12]$$

Cr is basically used to improve the corrosion resistance of stainless steels, although higher amounts of it may reduce their formability [12]. This phenomenon is said [13] due to the formation of ferrite and also sigma phase, and is confirmed by the above equations.

These equations also show that the effective coefficient of Mo is different. This element is not only a strong ferrite stabilizer, but also has a good resistance against pitting corrosion [9]. It is also efficient in promoting solid solution hardening and precipitation hardening during aging [14,15]. However higher amounts of this element is not suggested due to its ferrite stabilizing effect and its effect on sigma phase formation. The above mentioned factors and economical considerations would limit the high amount of these elements in stainless steels [9, 13].

Recently the investigations for obtaining high strength precipitation hardened stainless steels resulted in the development of a 12Cr-9Ni-4Mo-2Cu-1Ti steel namely of Sandvik 1RK91 [15]. This kind of steel is commonly used as thin wires in medical tools [16].

It is well known [17] that increasing the dimension of a product may reduce its mechanical properties. Up to now, no literature on the improvement of mechanical properties of this steel in the form of larger samples has been reported. In this work an attempt has been made to increase the dimension of the products, and the application of these steels, by achieving the optimum mechanical properties through varying its Cr and Mo contents.

2. EXPERIMENTAL PROCEDURES

The alloys were prepared by induction melting under an argon atmosphere, using ultra low Carbon Iron and high purity low Carbon ferroalloys. The ingots weighing about 10 kg were then refined by Electro Slag Remelting (ESR) Process. Two groups of xCr-4Mo-9Ni-2Cu-1Ti-1V with a Cr contents between 9-13 wt%, and yMo-10Cr-9Ni-2Cu-1Ti-1V alloys with a Mo contents between 3-6 wt%, here designated as Cr-steels and Mo-steels respectively were prepared. Their compositions are reported in Table 1. The compositions of these alloys are based on Sandvik 1RK91, with 1 wt% V addition.

Table 1. Chemical composition of the two types of steels investigated (wt%) xCr-9Ni-4Mo-2Cu-1Ti-1V & yMo-10Cr-9Ni-2Cu-1Ti-1V

Alloy	C	Cr	Ni	Mo	Cu	Ti	V	$Cr_{(eq)}$,Eq. 1(a)
9Cr	0.022	9.08	9.21	4.02	2.05	0.98	1.05	15
10Cr	0.021	10.18	9.32	4.05	2.08	1.02	1.01	16
11Cr	0.026	11.13	9.13	4.20	2.01	0.96	1.07	17
12Cr	0.021	12.14	9.01	4.11	1.97	0.95	1.08	18
13Cr	0.022	13.15	9.15	4.06	2.05	0.97	1.02	19
3Mo	0.22	10.09	9.83	3.06	2.02	.98	1.11	15
4Mo	0.021	10.18	9.32	4.05	2.08	1.02	1.01	16
5Mo	0.015	10.02	9.81	5.11	2.13	0.95	1.05	17
6Mo	0.023	10.21	9.79	6.04	2.06	1.01	1.14	18

After application of thermomechanical treatments of the alloys, the specimens were chemically etched in $30H_2O + 25CH_3OH + 40HCl + 5CuCl_2$ solution. Then their microstructure was examined by SEM. In addition, EDX and XRD with Cu-kα radiation were used for studying the microstructure.

The HV technique was also used for finding the hardness of the samples. Samples were cold rolled with a thickness reduction in the range of 10-90% and aged at 500^{o}C for 3 hours. Tensile tests were performed on the samples which cold rolled about 80% and then aged. The fracture surfaces of tensile specimens were also studied by SEM.

3. RESULTS AND DISCUSSION

3.1. Microstructure

Fig. 1 shows SEM images of Cr steels in solution treated condition. It is found that 9Cr steel has austenitic-martensitic structure, and Cr addition reduces martensite content. Murayama et al [18] reported that the uniform distribution of Mo, Cr and Ni atoms is an indication of a uniform solid solution of in an austenitic phase. Adding higher amounts of Cr to the steel, ferrite phase appears.

Results obtained by XRD analysis, shown in Fig. 2(a), indicate the presence of γ(111), γ(200), γ(220), γ(311) peaks and α(110), α(200), α(211), α(220) peaks in 9Cr steel. The former peaks are clearly revealed as austenite, but the second group of peaks can be either martensite or ferrite. Whereas the EDX analysis of the observed phases of 9Cr steel, presented in Table 2, does not show any difference in Cr and Mo steels areas of the structure in Fig. 1(a). Therefore α peaks must be martensite. Fig. 2(b) shows that the peak heights of γ phase 12Cr steel are higher than that of 9Cr steel. This confirms the increase in the stability of austenite in 12Cr steel. By the way, the EDX analysis represented in Table 2 shows that the amounts of Cr, Mo, and V in **C** areas are higher than that in **D** areas of Fig. 1(d). Therefore, the **C** areas observed in the mentioned figure, must be ferrite. The variation observed in the microstructure of Mo steels by adding Mo, is similar to Cr steels. Schefler diagram also confirms the above results. In other words, by considering Ni_{eq} to be 12 for these steels and calculating Cr_{eq} from Eq. 1(a), reported in Table 1, the structure of investigated steels is in the boundary region between three phases, austenite, martensite and ferrite. Formation of ferrite by adding ferrite stabilizing elements in stainless steels is also indicated by other researchers [9,13]. Additional support is presented by Goecman et al [19] on martensitic stainless steels with low amount of Mo and Ni. They argued that increasing amount of Cr from 9 to 12% caused the formation of delta ferrite in the range of 2-5%.

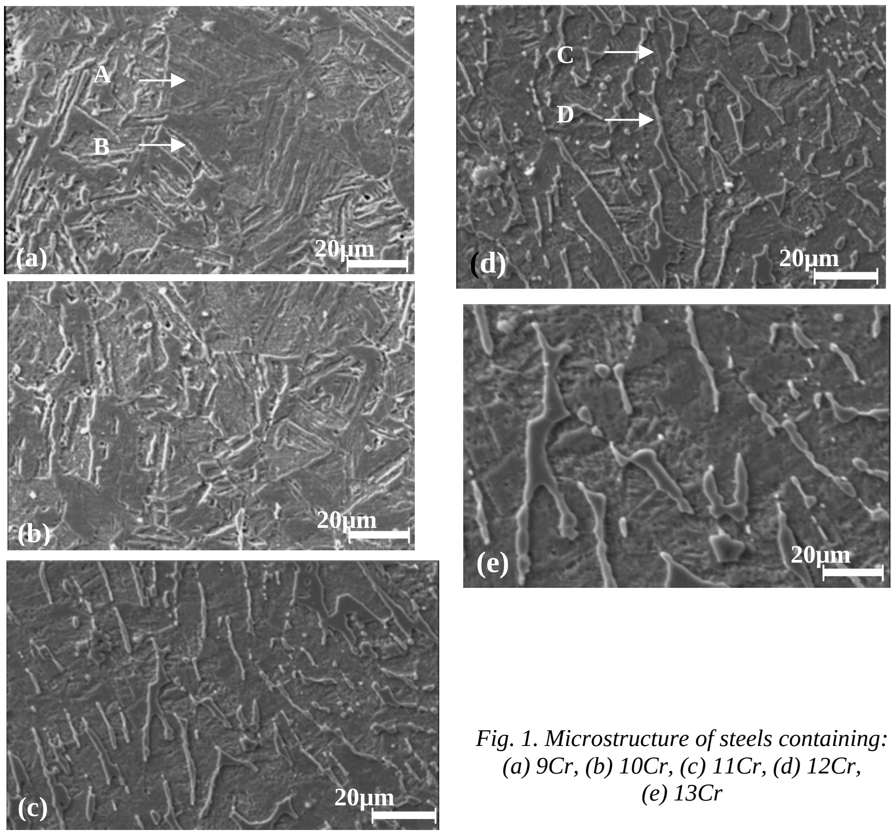

Fig. 1. Microstructure of steels containing: (a) 9Cr, (b) 10Cr, (c) 11Cr, (d) 12Cr, (e) 13Cr

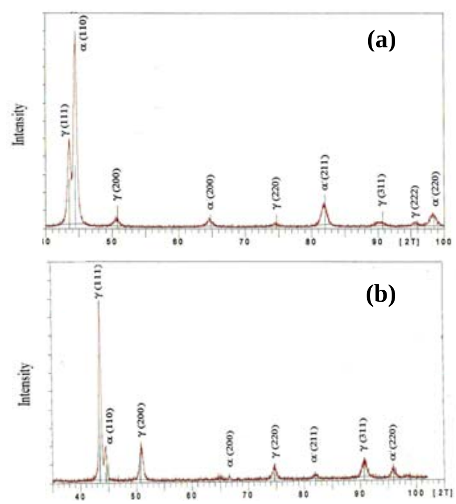

Fig. 2. X-ray diffraction patterns of hot rolled and solution treated steels containing: (a) 9Cr, (b) 12Cr

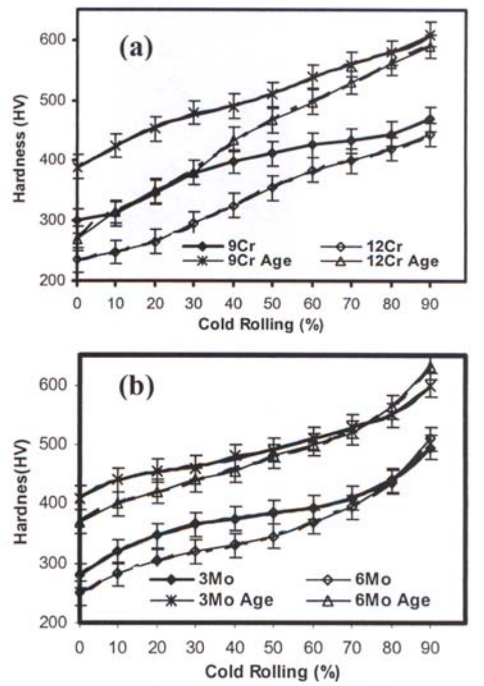

Fig. 3. Variation of hardness of rolled and aged steels containing: (a) 9Cr and 12Cr, (b) 3Mo and 6Mo

Table 2. EDX analysis of the constituent phases of 9Cr steel, Fig. 1(a), and 12Cr steel, Fig. 1(d)

Alloy	symbol	Cr	Ni	Mo	Cu	Ti	V
9Cr	A	8.95	9.82	4.17	2.11	1.11	0.97
	B	9.15	8.73	5.11	1.93	1.23	1.12
12Cr	C	11.83	10.38	3.36	2.28	1.22	0.88
	D	15.29	6.37	5.03	2.13	2.07	1.79

3.2. Cold rolling

The change in hardness by applying cold rolling is shown in Fig. 3 for four types of steel. It can be observed that, by applying plastic strain during cold rolling, hardness increases. The increase in hardness at the first stages is due to the transformation of austenite to ε and ά martensite. The contribution of cold rolling to the hardness increase at higher reductions is due to the improvement of the above reactions, transformation of ε martensite to ά martensite, work hardening effect and increasing the amount of dislocation density. Increasing volume fraction of precipitates during aging, by increment in the nucleation sites is the other positive effect of cold rolling in increasing strength.

XRD analysis of 12Cr steel after cold rolling with 80% reduction is shown in Fig. 4. The comparison of Fig. 4 with Fig. 2(b) for the solution treated specimens confirms the formation of ά martensite at higher amounts of deformation. The increase in the peak height of ά martensite, and the disappearance of austenite peaks, indicates the accomplishment of martensitic transformation.

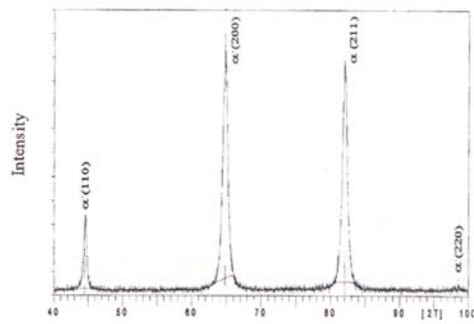

Fig. 4. X-ray diffraction patterns of 80% cold rolled 12Cr steel

At all stages of cold rolling, decreasing Cr and Mo contents, leads to an increase in the hardness of steels at primary and aged conditions. Especially, at higher amount of cold rolling, the difference in hardness reduced. As mentioned before, in steels with high amounts of austenite stabilizing elements, martensite does not form by cooling, but it is formed under applied stress or strain at temperatures lower than M_D. Studies [20] about the influence of alloying elements on M_D show that most of alloying elements cause the reduction in M_D and the increment in austenite stability. The relationship between the M_D temperature and the amount of alloying elements is reported as [20]:

$$M_{D30/50}(^{o}C) = 413 - 13.7Cr - 18.5Mo - 462(C+N) - 9.2Si - 8.1Mn - 9.5Ni \qquad (2)$$

For example, Cr and Mo would have a stabilizing effect on austenite, with a reducing coefficient of 13.7 and 18.5 degrees centigrade for one percent of Cr or Mo respectively. By replacing the chemical composition of these steels in equation (2), the M_D temperature for two groups of steels, represented in Table 3, will be in the range of 49-108 ^{o}C. Therefore cold rolling can result in the austenite to martensite transformation. However for 13Cr steel and 6Mo steel due to the little difference between the M_D temperature and the temperature of cold rolling (room temperature), austenite stability is higher. So the driving force for transformation is increased. Other studies on austenitic stainless steels [21] have arrived at a similar conclusion. Results show that in steels with higher amounts of M_D such as AISI 304 and AISI 301, the tendency to the formation of DIM at room temperature is increased, while the amount of DIM is reduced due to the lower amount of M_D in other austenitic stainless steels.

Table 3. The measured M_D temperature and SFE of steels with different amounts of Cr and Mo

Alloys	Cr steels (%)					Mo steels (%)			
	9Cr	10Cr	11Cr	12Cr	13Cr	3Mo	4Mo	5Mo	6Mo
M_D (^{o}C)	108	90	76	64	53	106	90	68	49
SFE (mJ/m^2)	48.1	48.8	49.5	49.7	50	43.7	48.8	62.7	70.8

In addition, the main alloying elements, Cr, Ni and Mo act chiefly in favor of strain induced transformation through their effect on the Stacking Fault Energy, SFE [22]:

$$SFE\ (mJ/m^2) = -53 + 9.3Mo + 0.7Cr + 6.2Ni + 3.2Mn \qquad (3)$$

Depending on the value of SFE, two different microstructures may be observed in the cold worked austenitic stainless steels [21,23]. For high SFE, a cellular distribution without DIM, and for low SFE, planar dislocation distribution containing DIM is seen. The SFEs of the investigated steels evaluated by means of equation (3), are reported in Table 3. It may be seen that, steels with low Cr and Mo contents have the lowest values of SFE. Therefore, their feature proves the larger amounts of DIM formed during cold rolling.

3.3. Aging

As shown in Fig. 3 the hardness increases during aging. The precipitates which are reported [15-17,24] to be formed during aging are Ni_3M (M=V-Mo-Nb-W), ηNi_3Ti, Fe_2Mo, δ, G, and X. At short times, Cu-rich precipitates are formed. A sequence of precipitation reactions which is reported by Hattestrand et al [17] involves Ni-rich precipitates nucleating at copper clusters followed by Mo-rich quasicrystalline precipitates and Ni-rich precipitates. In other words, at this stage Mo-rich precipitates have the major role in increasing strength. This behavior is due to the high resistance of Mo against overaging even if aging is done at 540 ^oC. On the other hand the alloys without any Mo show the increase in hardness only up to 425 ^oC. In addition, the distribution of precipitates is another effective factor in increasing hardness. Therefore stress fields around great number of very fine precipitates with uniform distribution can retard the dislocation motions and may results in the remarkable increase in hardness. It is found that at large reductions, the amount of hardness in the steel with higher Mo content is higher than the steel with lower one. In this condition, although the volume fraction of ferrite is increased, Mo plays an important role in increasing hardness by precipitation hardening.

3.4. Mechanical properties

Fig. 5 shows the changes in mechanical properties of the 80% cold rolled and aged Cr steels. Results show that yield strength and tensile strength increase, ductility does not change and index of strength – ductility balance increases by increasing Cr content up to 10%. Although the structure of 9Cr steel and 10Cr steel does not show any variation, the increase in solid solution hardening due to the increment in Cr content, may relate to this behavior. In 10Cr steel, presence of V, which is a strong ferrite stabilizer and a precipitation hardened element, leads to the highest mechanical properties. However the corrosion resistance of this steel is lower than the common stainless steels. By increasing Cr content, mechanical properties are decreased due to the ferrite formation. The most important point to be stated is that the strength – ductility balance is remained in the appropriate range. The transformation of austenite to martensite after 80% cold rolling, and the increase in strength by aging of the low Carbon martensite may lead to this result.

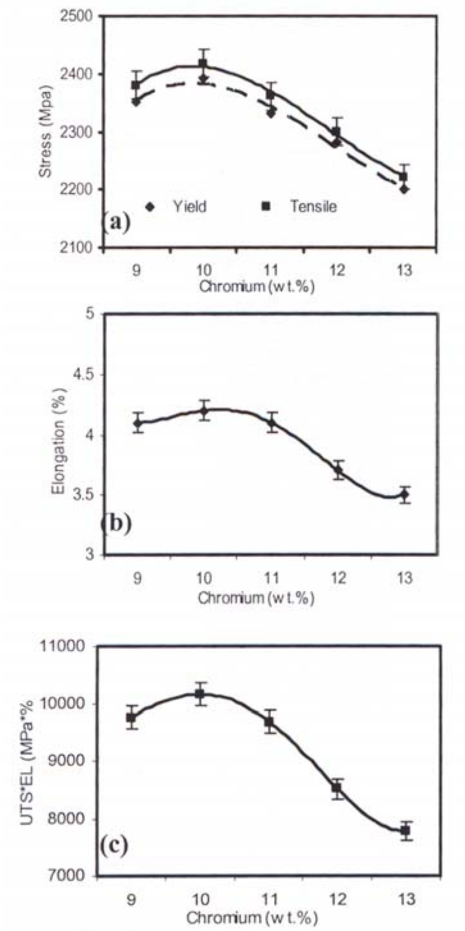

Fig. 5. Changes in mechanical properties as a function of Cr content in 80% cold rolled and aged steels: (a) yield strength and tensile strength, (b) elongation and (c) an index of strength – ductility balance

Fig. 6 shows the changes in yield strength and tensile strength (a), elongation (b) and an index of strength – ductility balance (c) of 80% cold rolled and aged Mo steels. It is clear that by increasing Mo content up to 6%, strength and ductility increase, so the index of strength – ductility balance increases remarkably. An explanation for such a behavior is that Mo has an accentuated effect in increasing solution hardening and consequently on work hardening and precipitation hardening. Moreover, Mo content of more than 5 wt% leads to the reduction in strength and ductility. Ferrite formation and the presence of undesirable precipitates such as sigma phase and Chi phase which their existence is reported in Mo bearing austenitic stainless steels [20], results in the decrease in mechanical properties. Similar conclusion has been reported by other researchers for the undesirable effect of ferrite on the hot formability of AISI 416 martensitic stainless steel [13] and the properties of a shape memory stainless steel [25].Whereas, some other works [9,26] show that the existence of certain amount of ferrite increases the corrosion resistance, and the impact toughness of ferritic stainless steels.

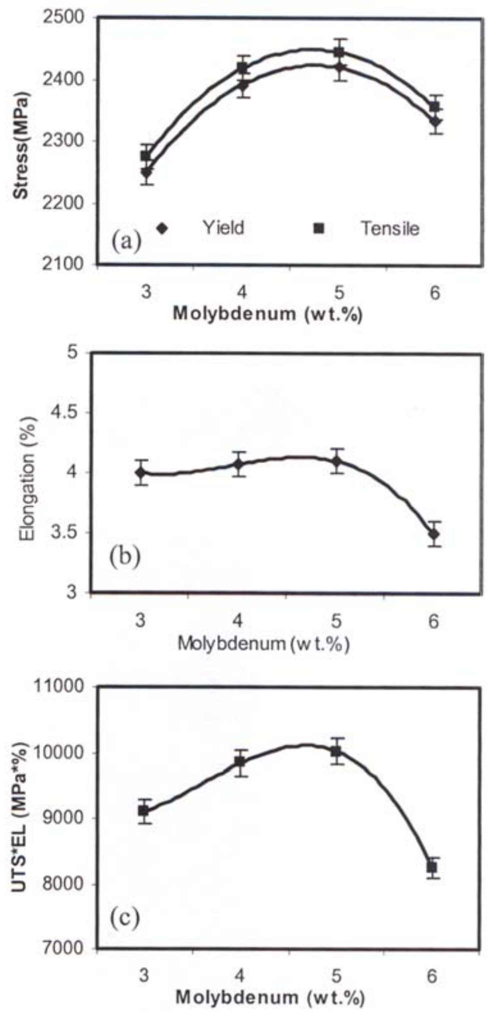

Fig. 6. Changes in mechanical properties as a function of Mo content in 80% cold rolled and aged steels: (a) yield strength and tensile strength, (b) elongation and (c) an index of strength ductility balance strength – ductility balance

3.5. Fractography

Fractographs of the steel 9Cr steel is shown in Fig. 7(a). As can be seen, the fracture surface is ductile, and fracture is caused by the nucleation of microvoids and their coalescence. However the fracture surface of 12Cr steel, Fig. 7(b), shows the remarkable decrease in the size of microvoids. In addition in some regions, cleavage areas are observed, that is the indication of brittleness character. The transition from ductile to brittle fracture surface is thought to be triggered by the activation of an incipient crack originating at ferrite. This may relate to the fact that the strength of ferrite is lower than that of austenite. The fracture route may be in the special directions, particularly from primary austenite grain boundaries.

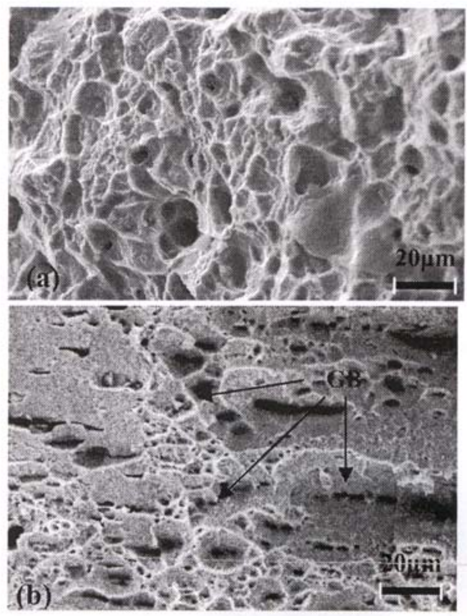

Fig. 7. The fractographs of tensile samples of steels containing: (a) 9Cr (b) 12Cr.

4. CONCLUSIONS

1. Both groups of steels containing different amounts of Cr and Mo have austenitic-martensitic structure after solution treating, but in steels with higher amounts of Cr and Mo, ferrite is started to form.

2. In all kinds of the steels investigated cold rolling leads to the austenite to martensite transformation.

3. By aging at 500 ^{o}C, the hardness of steels are improved, particularly in steels with lower Cr and higher Mo contents which cold rolled more.

4. In Cr steels, the hardness and strength follows an increasing trend and the ductility does not changed, with the addition of Cr content. This effect is particularly pronounced in 10Cr steel.

5. When the Mo content is 5%, mechanical properties are improved. If the Mo level is kept below or above 5%, these properties will be deteriorated.

6. The fractograph of 12Cr steel is more brittle than that of 9Cr steel, which is confirmatory to the detrimental effect of ferrite.

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